

# The Zintl–Klemm Concept Applied to Cations in Oxides.

## II. The Structures of Silicates

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**Abstract** The structures of ternary and quaternary silicates are revisited on the basis of the Zintl–Klemm concept and the Pearson's generalised octet rule. The three-dimensional skeletons formed by the Si atoms can be interpreted as if the Si atoms were behaving as

Zintl polyanions, adopting the structure of either main-group elements or Zintl polyanions showing the same connectivity. The O atoms are then located close to both, the hypothetical two-electron bonds and the lone pairs, giving rise to a tetrahedral coordination. In some silicates, the Si atoms clearly show an amphoteric character so that some Si atoms act as donors (bases) adopting an octahedral coordination, whereas others behave as acceptors (acid), adopting a tetrahedral coordination. Although the octahedral coordination seems to be favoured by the application of pressure, the results reported here indicate that the coordination sphere of silicon is not a function of the assumed ionic radius of the  $\text{Si}^{4+}$  cations but it depends on the nature of the other cations accompanying them in the structure.

**Keywords** Silicates · Structures · Zintl–Klemm concept · Cation arrays · Zintl phases

### Abbreviations

CN	Coordination Number
ELF	electron localisation function
HP	high pressure
HT	high temperature
NNM	non-nuclear maxima
P	pressure
PSE	Periodic Table of Elements
T	temperature
VSEPR	valence shell electron pair repulsion

## 1

### Introduction

The chemistry of silica and silicates has been widely studied. Silicates are the most interesting and the most complicated class of minerals. Approximately 30% of all minerals are silicates and some geoscientists estimate that 90% of the Earth's crust is made up of silicates. They also play an important role in daily life. Thus, silicates are present in raw materials and several industrial products such as glass, concrete and many ceramic materials. Their widespread application is due to the large variability of their properties and this, in turn, is due to the very large number of different silicate phases and the diversity of their structures.

Concerning the structural chemistry of silicates, the Inorganic Crystal Structure Database (ICSD), release 2004, contains 3192 entries of ternary and quaternary silicates. Silicates have often been described on the basis of the ionic model, i.e. a dense packing of  $\text{O}^{2-}$  anions in which  $\text{Si}^{4+}$  cations seem to fit into interstitial tetrahedral voids [1]. However, several experimental studies of the electron density distribution clearly indicate that the Si–O bond has a considerable covalent character [2]. Thus, a model which considers silicates as formed by either isolated or condensated  $[\text{SiO}_4]$  tetrahedra seems

to be more appropriate. Following this descriptive model, silicates have been classified into monosilicates, oligosilicates, ring silicates, chain silicates, layer silicates and tectosilicates according to the type of polyanion present in the structure. A richly illustrated survey of the structures of crystalline silicates is the book “*Structural Chemistry of Silicates*” which contains an extensive study of the bonding and structures of these compounds [3]. In it, the structures are classified and described following a criterion of increasing complexity of the silicate polyanions but it should be pointed out that the reasons why these polyanions adopt a given structure are far from being explained. This is the reason why the so-called “rich variety” of condensated silicate polyanions has been considered, in many instances, as “capricious”.

An early attempt to correlate, in tetrahedral structures, the connection between the tetrahedra and composition was carried out by Parthé & Engel [4]. Later, Parthé & Chabot [5] applied the Zintl–Klemm concept [6, 7] to deduce the connectivity in structures with anionic tetrahedron complexes of the general formula  $C_m C'_m A_n$ . From valence-electron criteria they deduced expressions which allow for the prediction of tetrahedral sharing numbers as well as the formation of  $C - C'$  and  $A - A$  bonds. Although they were able to predict connectivity between  $CA_4$  and  $C'A_4$  tetrahedra, the 3D frameworks remained unexplained and they were not related to other simple or elemental structures.

In a more recent paper [8], the Zintl–Klemm concept [6, 7] and Pearson's generalised octet rule [9] were successfully applied to 94 ternary aluminates, a family of compounds which, like silicates, also form condensated polyanions of tetrahedrally coordinated Al atoms. These two old concepts will help us to understand both the coordination spheres of the Si atoms and the three-dimensional arrays of their structures. Because some readers will not be familiar with these concepts, they will be briefly described in Sect. 3.

When this concept was applied to describe the Al-frameworks in aluminates, it was seen that, in aluminates of highly electropositive metals such as alkali, alkaline-earth and rare earth metals, the Al atoms form 3D skeletons which can be interpreted as if the Al atoms would behave as Zintl polyanions with hypothetical Al – Al bonds. These Al skeletons adopt the structure of either main group elements or Zintl polyanions showing the same connectivity. The O atoms are then docked close to both, the hypothetical Al – Al two-electron bonds and the lone electron pairs, giving rise to tetrahedral coordination of Al. On the contrary, when less electropositive (more electronegative) species coexist with aluminium in the oxide, the Al atoms do not behave as a Zintl polyanion anymore and adopt an octahedral coordination. Moreover, in some instances, the Al atoms exhibit their amphoteric character by which some of them act as electron donors towards other (acidic) Al atoms which behave as Zintl polyanions. In these cases, both types of coordination polyhedra, octahedra (donors) and tetrahedra (acceptors) coexist in the structure.

In the present work, our aim is to extend this study to some ternary and quaternary silicates. The Si subarray will be analysed in the light of both, the Zintl–Klemm concept [6, 7] and Pearson’s generalised octet rule [9]. It is well known that aluminates and silicates present many structural similarities. So, the principles applied to aluminates will be extended here to the structures observed in silicates, in order to provide an alternative view which puts all these apparently capricious structures on a common basis. Although we have carried out a systematic study of the structures of ternary and quaternary silicates, our aim is not to present a comprehensive study but rather to analyse some selected examples in the light of the Zintl–Klemm concept to demonstrate its applicability. To assist the reader in applying these principles to any other silicate structure, a more extended survey of silicates is given in Tables 3–7.

## 2

### The Crystal Chemical Formula Notation for Silicates

Throughout this article, when silicates are described, the term “coordination” will be used to denote how  $X^1$  anions (usually oxygen atoms) surround a given cation, and the term “connectivity” will be used to express, in particular, the contacts between tetrahedrally coordinated cations ( $T^1$  atoms) which are connected by a bridging oxygen forming Si – O – Si bonds. When the imaginary Si atom skeleton of a silicate structure is described, the term Si – Si will be used to denote the link between two Si atoms that in the actual silicate represents a Si – O – Si bond. It will be seen below that for many silicates the Si atom skeleton is topologically very similar to the structures of corresponding, existing or hypothetical, Zintl phases in which the Si – Si link of the skeleton is replaced by a real Si – Si bond.

Silicates will be described following an increasing order of structural complexity. We will begin with monosilicates, passing to oligosilicates, ring silicates, chain silicates, layer silicates to end with tectosilicates, most of which are quaternary compounds where silicon, together with other T atoms, like B, Be, Al, etc. and oxygen atoms are forming the tetrahedral frameworks. All cations which, together with oxygen or other anions, are forming these tetrahedral frameworks will be denoted by the symbol T and consequently, the skeleton formed by the connected T atoms will be denoted as the T atom framework or T atom skeleton. Because the Zintl–Klemm concept establishes

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<sup>1</sup> Following a recent recommendation to write chemical formulas containing structural information [10], in this paper distinction is made between the usual *element symbols* such as Si, Al, O, Cl, etc. (given as normal face Latin letters) and *structure-site symbols* (given as boldface Latin letters) such as T for tetrahedrally coordinated cations, A for cations without regard to their coordination number, X and Y for monoatomic anions, Z for polyatomic anions, and M for molecules such as H<sub>2</sub>O, CO<sub>2</sub>, etc.

the relationship between the connectivity of the atoms and their chemical properties, a knowledge of the crystal structure of the compound under consideration is required. Crystal chemical formulas are very efficient short-hand descriptions of both, chemical composition and structure of a substance. The crystal chemical formulas used in this paper are those recommended by the Commission on Crystallographic Nomenclature of the International Union of Crystallography [11].

Rather than giving the complete structural formula of a general inorganic compound, the formula notation shall be explained here for two typical silicates:

- Tremolite is an amphibole of chemical composition  $\text{Ca}_2\text{Mg}_5[\text{Si}_4\text{O}_{11}]_2(\text{OH})_2$  [12]. Its main structural features can be given as  $\text{Ca}_2^{[8]}\text{Mg}_5^{[6]}\{\text{uB}, 2, 2_\infty^1\}[\text{Si}_2^{[1;3]}\text{Si}_2^{[1;2]}\text{O}_{11}]_2(\text{OH})_2$ .
- The structure of turkestanite,  $\text{K}_{<1}(\text{Na}, \text{Ca})_2\text{Th}[\text{Si}_8\text{O}_{20}]$ , [13] can be written as  $\text{K}_{<1}^{[12]}(\text{Na}, \text{Ca})_2^{[8]}\text{Th}^{[8]}\{\text{uB}, 4, 2r\}[\text{Si}_8^{[1;3]}\text{O}_{20}]$ .

These two specific formulas can be generalised into the following crystal chemical formula of silicates  $\text{A}_a^{[\text{CN}]}\text{A}_{a'}^{[\text{CN}]}\dots\{\text{B}, \text{P}, \text{M}_\infty^{\text{D}}\}[\text{T}_t^{[l;s]}\text{T}_{t'}^{[l;s]}\dots\text{X}_x, \text{X}_{x'}]\text{Y}_y\text{Z}_z(\text{M}_m)$ .

In this formula the silicate anion is written within square brackets and its constitution within the preceding curly brackets. Cations not belonging to the silicate anion precede, and non-silicate anions follow the information on the silicate anion. If necessary, coordination numbers can be written, within square brackets, as trailing superscripts to the element symbols. Usually only four-coordinated cations (T cations) are considered as part of a silicate anion. Therefore, it is unnecessary to add the coordination numbers as a trailing superscript to the T cations.

The information on the constitution of the silicate anion contains (i) the branchedness **B** which may be unbranched (**uB**), open-branched (**oB**), loop-branched (**lB**), open- as well as loop-branched (**olB**) or hybrid (**hB**); (ii) the periodicity, i.e. the number of tetrahedra in the identity period of the fundamental chain (**P<sup>C</sup>**) or fundamental ring (**P<sup>R</sup>**) from which the silicate anion can be generated by successive linkage; (iii) the multiplicity **M** of the silicate anion; and (iv) its dimensionality **D** which is the number of dimensions in which the silicate anion has infinite extension. Oligoanions and rings, both having **D** = 0, can be distinguished as **t** and **r** (for terminated and ring-shaped anions, respectively).

The tetrahedrally coordinated T cations forming, together with the X anions, the silicate anions, can be characterised by two parameters, the linkedness (**l**) and the connectedness (**s**). The linkedness (**l**) expresses the number of X atoms (usually oxygen and only in rare cases, nitrogen) shared with each adjacent T cation. Thus, **l** = 0 for isolated tetrahedra, **l** = 1 for corner-sharing tetrahedra and **l** = 2 for edge-sharing tetrahedra. The connectedness (**s**) accounts for the number of adjacent T cations with which a given T cation

shares common X atoms. Thus, for a corner-connected network,  $s$  is the number of corners shared by a given  $[\text{SiO}_4]$  tetrahedron. It is the value of  $s$  which is most relevant in connection with the Zintl–Klemm concept. The maximum possible value of  $s$  is 4 for a Si or  $\Psi$ -Si atom, 3 for a P or  $\Psi$ -P atom, 2 for S or  $\Psi$ -S and 1 for  $\Psi$ -Cl. For more detailed information on the parameters used for the formula notation see [3].

For silicate anions of finite extension ( $D = 0$ ), the total number of T and X atoms ( $\sum t$  and  $\sum x$  respectively), to be given between the square brackets of the crystal chemical formula, are equal to the numbers of these atoms in the anion. For silicate chains ( $D = 1$ ),  $\sum t$  is the number of T atoms in one identity period of the chain. For silicate anions with  $D > 1$ , the numbers of atoms are usually chosen in such a way that  $\sum t$  is the smallest multiple of the T atoms in the period of its fundamental chain for which  $\sum x$  is an integer.

According to this information, the structural formula of tremolite given above indicates that its silicate anion is an unbranched *zweier* double chain in which half of the Si atoms are 2-connected and the other half are 3-connected. In analogy, the formula given for turkestanite indicates that its silicate anion is an unbranched *vierer* double ring in which all its Si atoms are 3-connected.

### 3

#### The Zintl–Klemm Concept

The Zintl concept [6], later extended by Klemm [7], was formulated in the 1930s and has been considered by Hoffmann [14] as “the single most important theoretical concept in solid-state chemistry of the last century”. It accounts for the structural and bonding features in the so-called Zintl phases ( $A_nX_m$ ) which are combinations of very electropositive metals (alkali, alkaline earth and rare earth metals) (A) with the main-group elements (X). The Zintl concept interprets the structure of these compounds as if the A atoms transfer their valence electrons to the X atoms. The X atoms, far from being individual anions, then form polyanionic skeletons in which they are bonded by directed, covalent X – X bonds. These bonds are formed by all the valence electrons, i.e., their own electrons plus those transferred from the A atoms, and the number of bonds formed obey the 8- $N$  rule ( $N$  being the number of valence electrons of the X atom). In other words, the X atoms tend to complete the octet in their valence shell. When heterogeneous X species are formed, then the X skeleton can be explained by the generalised octet rule [9].

Klemm [7] proposed the pseudo-atom concept for the charged  $X^{n-}$  atom that would adopt a structure characteristic of the isoelectronic main group element. To illustrate the Zintl–Klemm concept, we will consider the compound NaSi. In this compound, each Na atom would transfer one valence electron to a Si atom converting it structurally into a pseudo-P atom ( $\Psi$ -P).

For this reason, in NaSi, the  $\text{Si}^-$  anions form  $[\text{Si}_4]^{4-}$  tetrahedra, similar to the molecules of  $\text{P}_4$ . The combination of Zintl's original concept and Klemm's pseudo-atom description, is called the Zintl–Klemm concept. Throughout this article, we will use the prefix  $\Psi$  to denote a pseudo-atom. Thus, taking again NaSi as an example, the  $\text{Si}^-$  anion can be denoted as  $\Psi\text{-P}$ .

It should be emphasised that, in the Zintl phases, two types of bonds co-exist. On one hand, the  $A - X$  interaction is assumed to be almost completely ionic. On the other hand, a directed, covalent bond is formed between the  $X$  atoms, giving rise to the formation of  $X_y^{n-}$  polyanions. As said by Schäfer [15], “ionic and covalent bonds in intermetallic phases were a matter of course for Zintl”. Like in other structures of the main group elements, such as Si, P, S, As, etc., the  $X$  atoms are bonded by directed, two-centre, two-electron bonds. In the same manner, the electrons not involved in bonds are located in non-bonding regions forming the so-called lone electron pairs. These lone electron pairs, together with the bonding electron pairs, normally form tetrahedral arrangements as has been shown in an electron density study on the  $\text{S}_8$  molecule [16]. Also, theoretical calculations of the Electron Localisation Function (ELF) carried out for  $\text{CaAl}_2\text{Si}_2$  [17] and for the butterfly-shaped  $\text{Si}_4^{6-}$  polyanion [18] reveal that occupied bonding and non-bonding states are always centred at  $X$  atoms. ELF calculations clearly show that the charge is localised in both, the bonding and the lone pair regions. The reader can find additional information concerning theoretical calculations and bonding aspects on the Zintl phases in [18, 19].

Another aspect to be dealt with here is to define which elements are capable of forming Zintl polyanions. In Table 1, part of the Periodic Table of Elements (PSE) with the elements near the Zintl border are presented. This line separates the metametals (Group 13 elements) from the semimetals and semiconductors which are the most common components of the Zintl phases. However, other elements at the left of this Zintl line, like Cd, Ag, Al, Ga, In and Tl, are also susceptible to forming Zintl polyanions. Comprehensive reviews of the work reported on such compounds can be found in [20, 21].

**Table 1** Partial representation of the Periodic Table showing the Zintl border which is represented by the *double vertical line* which separates the Groups 13 and 14

11	12	13		14	15	16
		Al		Si	P	
Cu	Zn	Ga		Ge	As	Se
Ag	Cd	In		Sn	Sb	Te
Au	Hg	Tl		Pb	Bi	Po

### 3.1

#### The Pseudo-Formula Notation for Zintl Phases

Throughout this article, the term pseudo-formula ( $\Psi\text{-Si}_k\text{P}_l\text{S}_m\text{Cl}_n$ ) will be used to denote the number of atoms which have been converted into each kind of  $\Psi$ -atom by acceptance of electrons from the more electropositive atoms. This  $\Psi$ -atom formula can be easily derived from the silicate formula by replacing each  $\text{T}^{[1;4]}$ ,  $\text{T}^{[1;3]}$ , ...,  $\text{T}^{[1;0]}$  atom by a  $\Psi\text{-Si}$ ,  $\Psi\text{-P}$ , ...,  $\Psi\text{-Ar}$  atom, respectively.

## 4

### The Main Group Elements and their Oxides

A common structural feature of the oxides of the main group elements is that they maintain the structure of either (i) the parent element; (ii) an element of its own group or; (iii) Zintl polyanions isoelectronic with them. The oxides are summarised in Table 2 together with the elemental structures recognisable in them. Although the reader can get an extensive insight into this phenomenon by examining Table 2, we will briefly describe some examples which will help to understand the behaviour of the silicate polyanions described below.

The best-known examples are the different polymorphs of  $\text{SiO}_2$ . Thus, cristobalite and the related compounds  $\text{GeO}_2$ ,  $\text{BPO}_4$ ,  $\text{BeSO}_4$  and the high temperature (HT) polymorph of  $\text{ZnSO}_4$ , all of them have a cationic array identical to either, the elements (diamond-like Si and Ge) or the corresponding zincblende-like (sphalerite-like) binary compounds BP, BeS and ZnS. In tridymite, the Si atoms adopt the same structure as lonsdaleite (sometimes called hexagonal diamond) and hexagonal silicon. The structure of quartz, adopted also by  $\text{GeO}_2$ ,  $\text{CO}_2$  under pressure [22],  $\text{BPO}_4$  and  $\text{AlPO}_4$ , has a cation array whose structure is identical to that of the Si-rich phase  $\text{CrSi}_2$  [23] and also to the cinnabar-like structure of the high-pressure phase of  $\text{ZnTe}$  [24]. Both structures are represented in Fig. 1. As pointed out by Wells [[25], p 131], the Si-subarray of keatite corresponds to the high pressure (HP) phase  $\gamma\text{-Ge}$  [26]. In stishovite, a HP phase of  $\text{SiO}_2$  [27], and in the isostructural compounds  $\text{GeO}_2$ ,  $\text{SnO}_2$  and  $\beta\text{-PbO}_2$ , the cations adopt the structure of an element of their Group, the HP phase  $\gamma\text{-Sn}$  [28]. Finally, the similarities between the Si array in both, the Zintl phase  $\text{K}_8\text{Si}_{46}$  [29] and the silica-framework of the microporous mineral melanophlogite have also been pointed out [30].

An important aspect of all these structures, is the location of the O atoms. It is well known that in all the elemental structures just described (with the exception of  $\gamma\text{-Sn}$ ), the Group 14 atoms are linked by directed, two-centre,



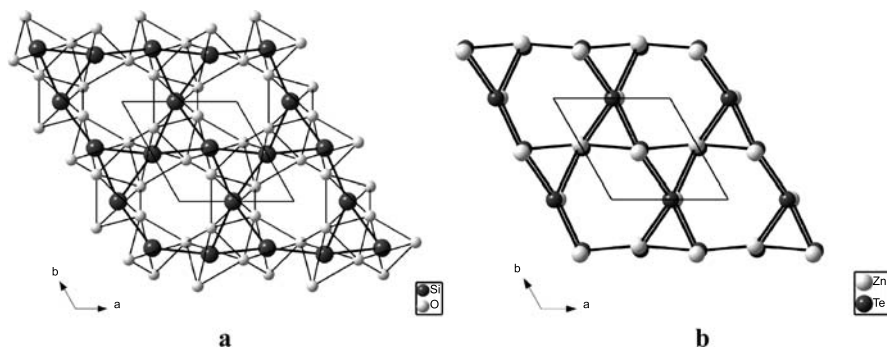
**Table 2** List of binary oxides of the main group elements whose cation subarray structures coincide topologically either with those of the elements of the same group or with Zintl polyanions showing the same connectivity. In the case of silica polymorphs, some isostructural ternary oxides have been included because they also maintain the structures of their respective alloys

Oxides preserving the elemental structures	Ref.	Elemental or alloy structures	Ref.
SiO <sub>2</sub> (cristobalite)	[119]		
GeO <sub>2</sub>	[120]	Si (diamond)	[125]
BPO <sub>4</sub>	[121]	BP	[126]
AlPO <sub>4</sub>	[122]	BeS	[127]
BeSO <sub>4</sub>	[123]	ZnS (blende)	[128]
ZnSO <sub>4</sub> (HT)	[124]		
SiO <sub>2</sub> (tridymite)	[129]	C	[131]
AlPO <sub>4</sub>	[130]	Si (hexagonal)	[132]
SiO <sub>2</sub> (quartz)	[133]		
GeO <sub>2</sub>	[134]		
CO <sub>2</sub>	[135]	CrSi <sub>2</sub>	[139]
BPO <sub>4</sub>	[136]	ZnTe (HP)	[140]
AlPO <sub>4</sub>	[137]		
FePO <sub>4</sub>	[138]		
SiO <sub>2</sub> (keatite)	[141]	γ-Ge (HP)	[142]
SiO <sub>2</sub> (stishovite)	[143]		
GeO <sub>2</sub>	[144]	γ-Sn (HP)	[146]
SnO <sub>2</sub>	[144]		
β-PbO <sub>2</sub>	[145]		
Melanophlogite (silica clathrate)	[147]	K <sub>4</sub> Si <sub>23</sub>	[148]
AlPO <sub>4</sub> ·2H <sub>2</sub> O (metavariscite)	[149]	CrB <sub>4</sub>	[150]
		β-BeO	[151]
AlPO <sub>4</sub> ·2H <sub>2</sub> O (variscite)	[152]	Si (HP)- related	[153]
P <sub>4</sub> O <sub>6</sub>	[154]		
P <sub>4</sub> O <sub>8</sub>	[155]		
P <sub>4</sub> O <sub>9</sub>	[156]		
P <sub>4</sub> O <sub>10</sub>	[157]	P <sub>4</sub> (molecules)	[161]
As <sub>4</sub> O <sub>6</sub>	[158]		
Sb <sub>4</sub> O <sub>6</sub>	[159]		
Sb <sub>4</sub> O <sub>10</sub>	[161]		
P <sub>2</sub> O <sub>5</sub>	[162]	CaSi <sub>2</sub> (HP)	[163]
		SrSi <sub>2</sub> (HP)	[163]
		BaGe <sub>2</sub>	[164]
		ThSi <sub>2</sub>	[165]
P <sub>2</sub> O <sub>5</sub>	[166]	As (layers)	[168]
As <sub>2</sub> O <sub>3</sub>	[167]	CaSi <sub>2</sub>	[169]

Continued on next page

**Table 2** (continued)

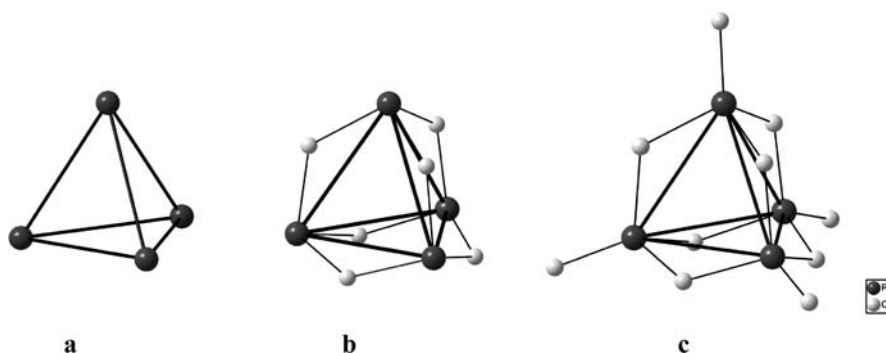
Oxides preserving the elemental structures	Ref.	Elemental or alloy structures	Ref.
As <sub>2</sub> O <sub>5</sub>	[170]	SrSi <sub>2</sub>	[171]
Sb <sub>2</sub> O <sub>5</sub>	[172]	Sb (HP)	[175]
Sb <sub>2</sub> O <sub>4</sub>	[173]	Bi	[176]
Bi <sub>2</sub> O <sub>4</sub>	[174]		
SO <sub>3</sub>	[177]		
SeO <sub>2</sub>	[178]	S (chains) asbestos-like	[181]
Se <sub>2</sub> O <sub>5</sub>	[179]	Se	[182]
$\gamma$ -TeO <sub>2</sub>	[180]	Te	[183]
S <sub>3</sub> O <sub>9</sub>	[184]	S <sub>3</sub> (molecule)	[185]
Se <sub>4</sub> O <sub>12</sub>	[186]	S <sub>4</sub> (molecule)	[187]
TeO <sub>3</sub>	[188]	Te (HP)	[189]
		Po	[190]
TeO <sub>2</sub>	[191]	S <sub>2</sub> (molecule)	[192]



**Fig. 1** **a** Projection of quartz structure in which the Si – Si contacts have been drawn with *thick lines* to show its similarity with **b** the structure of HP-ZnTe

two-electron bonds and, when an oxide is formed from the element, the O atoms are always located close to the midpoints of these bonds, maintaining the topology of the elemental structure and producing thus a tetrahedral coordination of the O atoms around the T atoms.

Regarding the Group 15 elements, this behaviour is kept. Thus, the tetrahedral structure of the P<sub>4</sub> molecule is preserved in the oxides P<sub>4</sub>O<sub>6</sub>, P<sub>4</sub>O<sub>8</sub>, P<sub>4</sub>O<sub>9</sub>, P<sub>4</sub>O<sub>10</sub>, As<sub>4</sub>O<sub>6</sub> (arsenolite), Sb<sub>4</sub>O<sub>6</sub> and Sb<sub>4</sub>O<sub>10</sub>. This behaviour had already been pointed out by Addison in 1965 [31]. Some of these structures are presented in Fig. 2.



**Fig. 2** The structure of the  $P_4$  molecule to show how it is maintained in the  $P_4O_6$  and  $P_4O_{10}$  oxides

The same occurs with a second  $P_4O_{10}$  phase, o- $P_4O_{10}$  (*Fdd2*), in which the  $[PO_4]$  tetrahedra form a 3-dimensional framework [32] whose P atom skeleton is similar to the arrangement of the Si atoms ( $\psi$ -P) in the Zintl phase  $SrSi_2$ . In the same manner, both, a third phase of  $P_4O_{10}$  (*Pnma*) [33] and a second phase of  $As_4O_6$  (claudetite) [34] maintain the layer structure of elemental As.

Also in these compounds, when the oxide is formed, the O atoms are located close to both, the P – P bonds and the lone pairs of the P (As) atoms. In this way, in the pentavalent oxides, the tetrahedral coordination is achieved.

At present we cannot give a completely rigorous explanation of why the basic geometric features of the structures of the elements are maintained in binary oxides although the distances between the element atoms are increased considerably. If we take the molecule of  $P_4O_6$  as a reference, it is clear that the insertion of oxygen into the  $P_4$  molecule leads to the formation of strong P – O covalent bonds, and thereby preventing the formation of significant phosphorus-phosphorus bonding interactions. A possible explanation of that coincidence could be that, in spite of the strong P – O bonds, some residual P – P interaction persists. However, this would require the potential energy surface to be very flat so that the very small bonding interaction energy could lead to such a preferred geometric arrangement. In this sense, theoretical calculations, including a topological analysis of the electron density, would be desirable in order to detect possible critical points between the P atoms. An alternative explanation is that the tetrahedral arrangement of the P atoms could reflect a minimum energy situation for two quite unrelated electronic situations. It is well known that certain polyhedral arrangements on the surface of a sphere are solutions both to the minimisation of repulsion and covering problems. Therefore, the observation of a tetrahedral arrangement in both cases may not have related electronic causes. Indeed they may have quite contradictory origins. Taking the VSEPR theory as a guide, the tetrahedral coordination minimises repulsions between the ligands (O atoms)

in phosphate and sulphate anions but at the same time it occurs in clusters such as  $P_4$  and  $B_4Cl_4$ , where significant element-element bonding is present. The tetrahedral arrangement of the phosphorus or boron atoms enables four atoms on the surface of a sphere to overlap and share electron density in the most efficient way. The tetrahedral arrangement also minimises the repulsions between four equal atoms on the surface of a sphere. Therefore, the same polyhedral geometry represents the most favoured solution for two quite different electronic situations. The octahedron and icosahedron display similar dual geometric solutions to the covering and repulsion problem.

The question which arises is whether these explanations can be extended to all the oxides of the main group elements. Without being able to resolve the electronic basis of these relationships the general observation remains that the O atoms in the compounds reviewed in this paper are always located in the vicinity of the electron pairs of the parent structure of the element. A “freezing” of the elemental structure is therefore observed when the elements are oxidised and the oxide anions are located in the regions of high electron density in the element. Although we have sought to explain the structures in terms of thermodynamic preferences, it could be that there is also a kinetic effect which results in the retention of the parent structure as the reaction proceeds, because the activation energies for such processes leading to these symmetric structures are lower than those for alternative reactions which lead to other structural rearrangements. Therefore, the freezing of the structure may have its origins in the mechanistic pathway leading to their formation.

In support of this generalisation, we refer to the theoretical calculations carried out on suboxides of Zintl phases [35]. The compound  $Ca_4Sb_2O$  [36] was first described as a binary calcium antimonide  $Ca_4Sb_2$  [37]. The structure contains isolated  $Sb^{3-}$  anions and the compound can only have the expected valency relationships if an additional  $X^{2-}$  anion is present. The additional anion was identified as  $O^{2-}$  and was located at the centre of a  $Ca_6$  octahedron. In fact, the calculation of the ELF for  $Ca_4Sb_2$  (without the O atom) produced only one additional localisation region at the centre of the  $Ca_6$  octahedron, just the position occupied by the additional O atom.

## 5 Silicates

As it has been reported for the aluminates [8], the application of the Zintl-Klemm concept to silicates turns out to be reasonable for the following reasons: on one hand because the main group elements maintain their structures when they form their corresponding oxides. On the other hand, because silicon is a Zintl element which, in the presence of very electropositive cations, behaves as a Zintl polyanion which can adopt the structure of other main

group elements whose networks, as it occurs with the binary oxides, can be maintained as well in the silicate anions.

Next, the structures of silicates will be analysed in the light of these concepts. The selected compounds are collected in Tables 3 to 7. Examples of silicates are selected such that the application of the Zintl–Klemm concept to the large variety of silicate structures is elucidated and can be comprehended. Following the rules given in Sect. 2, the concise formulas can be developed into more detailed structural ones by considering the chain periodicity  $P^C$  and distinguishing the T atoms according to the values of  $k$ ,  $l$ ,  $m$  and  $n$  of their pseudo-atoms. For example, the formula of the unbranched zweier double chain silicate tremolite  $\text{Ca}_2\text{Mg}_5[\text{Si}_4\text{O}_{11}]_2(\text{OH})_2$  can be extended to  $\text{Ca}_2^{[8]}\text{Mg}_5^{[6]}\{\mathbf{uB}, 2, 2_\infty^1\} [\text{Si}_2^{[1;3]}\text{Si}_2^{[1;2]}\text{O}_{11}]_2(\text{OH})_2$ .

References to examples listed in Tables 2–7 are given with small letters a, b, ... if heterochemical silicates with the same general formula but different cations A, A', etc. are listed. Underlined element symbols indicate that a mineral name is given. For several mineral groups with a large number of members, no reference is given. Phases for which no mineral name is given in Tables 3–7 have been synthesised but not found in nature. In the text and in the tables, reference is made to the most recent and most accurate crystal structure refinements.

## 5.1

### Monosilicates

Monosilicates are characterised by the existence of isolated  $[\text{SiO}_4]^{4-}$  anions. To this family of compounds belong very common minerals such as olivines  $\text{A}_2[\text{SiO}_4]$  ( $\text{A}^1 = \text{Mg, Mn, Fe, Co, Ni}$ ), spinels, garnets  $\text{A}_3\text{A}'_2[\text{SiO}_4]_3$  (with  $\text{A} = \text{Mg, Ca, Mn, Y, ...}$ ,  $\text{A}' = \text{Al, Fe, Cr, V, ...}$ ), apatite-like silicates such as  $\text{Ca}_3\text{Y}_2[\text{SiO}_4]_3$  and  $\text{Y}_5[\text{SiO}_4]_3\text{N}$ , zircon  $\text{Zr}[\text{SiO}_4]$ , etc. In addition to these compounds, more than one hundred quaternary phases have been described, among them, compounds in which non-silicate anions coexist with the monosilicate anions.

In terms of the Zintl–Klemm concept, a  $[\text{SiO}_4]^{4-}$  anion can be derived from a  $\text{Si}^{4-}$  anion, if electropositive atoms are able to transfer four electrons to the Si atom. The  $\text{Si}^{4-}$  anion has a noble gas configuration, ( $\psi$ -Ar), with four pairs of electrons in its valence shell. Now, if each of the electron pairs of a Si atom is approached by an O atom, the monosilicate anion is formed. Thus, in  $\text{Mg}_2[\text{SiO}_4]$ , the two Mg atoms per formula unit would transfer four electrons to the Si atom, converting it into  $\text{Si}^{4-}$ , with a noble gas configuration.

## 5.2

### Oligosilicates

A selection of oligosilicates  $\text{A}_a\text{A}'_{a'} \dots \{\mathbf{t}\}[\text{Si}_n\text{O}_{3n+1}]\text{Y}_y\text{Z}_z$  is given in Table 3.

**Table 3**

Mineral name	Oligosilicates Disilicates $\{^0_\infty\}$ Pseudo-Cl <sub>2</sub>	Ref.
	Formula	
Suolunite	H <sub>2</sub> Ca <sub>2</sub> [Si <sub>2</sub> O <sub>7</sub> ](H <sub>2</sub> O)	[193]
	Li <sub>2</sub> Cu <sub>5</sub> [Si <sub>2</sub> O <sub>7</sub> ] <sub>2</sub>	[194]
	Na <sub>2</sub> Si <sup>[6]</sup> [Si <sub>2</sub> O <sub>7</sub> ]	[195]
	K <sub>6</sub> [Si <sub>2</sub> O <sub>7</sub> ]	[196]
	Rb <sub>2</sub> Be <sub>2</sub> [Si <sub>2</sub> O <sub>7</sub> ]	[197]
Edgarbaileite	A <sub>6</sub> [Si <sub>2</sub> O <sub>7</sub> ] with A = Ag, <u>Hg</u> (I), Tl(I)	[198a–c]
Bertrandite	Be <sub>4</sub> [Si <sub>2</sub> O <sub>7</sub> ](OH) <sub>2</sub>	[199]
Barylite, clinobarylite	Be <sub>2</sub> Ba[Si <sub>2</sub> O <sub>7</sub> ]	[200a–b]
Rankinite	Ca <sub>3</sub> [Si <sub>2</sub> O <sub>7</sub> ]	[201]
Cuspidine	Ca <sub>4</sub> [Si <sub>2</sub> O <sub>7</sub> ]F <sub>2</sub>	[202]
Wadsleyite	Mg <sub>4</sub> [Si <sub>2</sub> O <sub>7</sub> ]O	[203]
	Ca <sub>2</sub> Y <sub>2</sub> [Si <sub>2</sub> O <sub>7</sub> ]O <sub>2</sub>	[204]
Gittinsite	CaZr[Si <sub>2</sub> O <sub>7</sub> ]	[205]
Baghdadite	Ca <sub>3</sub> Zr[Si <sub>2</sub> O <sub>7</sub> ]O <sub>2</sub>	[206]
Andremerite	BaFe <sub>2</sub> [Si <sub>2</sub> O <sub>7</sub> ]	[207]
Fresnoite	Ba <sub>2</sub> Ti[Si <sub>2</sub> O <sub>7</sub> ]O	[208]
	Ba <sub>2</sub> Mn(III) <sub>2</sub> [Si <sub>2</sub> O <sub>7</sub> ]O <sub>2</sub>	[209]
Belkovite	Ba <sub>3</sub> Nb <sub>6</sub> [Si <sub>2</sub> O <sub>7</sub> ] <sub>2</sub> O <sub>12</sub>	[210]
Hemimorphite	Zn <sub>4</sub> [Si <sub>2</sub> O <sub>7</sub> ](OH) <sub>2</sub> (H <sub>2</sub> O)	[211]
	Al <sub>3</sub> [Si <sub>2</sub> O <sub>7</sub> ](OH) <sub>3</sub>	[212]
	Y <sub>4</sub> [Si <sub>2</sub> O <sub>5</sub> N <sub>2</sub> ]O <sub>2</sub>	[213]
	In <sub>2</sub> [Si <sub>2</sub> O <sub>7</sub> ]	[214]
Thortveitite, yttrialite, keiviite	A <sub>2</sub> [Si <sub>2</sub> O <sub>7</sub> ] with A = <u>Sc</u> , <u>Y</u> , La, Ce, Pr, Nd, Sm, Eu, Gd, Ho, Er, <u>Yb</u>	[215a–q]
	A <sub>3</sub> [Si <sub>2</sub> O <sub>7</sub> ]Cl <sub>3</sub> with A = La, Pr	[216a–b]
	Si <sup>[6]</sup> [P <sub>2</sub> O <sub>7</sub> ]	[217a–d]
	Unbranched Trisilicates $\{^0_\infty\}$ Pseudo-SCl <sub>2</sub>	
	H <sub>2</sub> K <sub>3</sub> A[Si <sub>3</sub> O <sub>10</sub> ] with A = Y, Tb, Eu(III)	[218]
	Er, Tb, Gd	
Rosenhahnite	H <sub>2</sub> Ca <sub>3</sub> [Si <sub>3</sub> O <sub>10</sub> ]	[219]
	A <sub>3</sub> [Si <sub>3</sub> O <sub>10</sub> ]F with A = Y, Dy, Ho, Er	[220a–b]
	Unbranched Tetrasilicates $\{^0_\infty\}$ Pseudo-S <sub>2</sub> Cl <sub>2</sub>	
Ruizite	H <sub>2</sub> Ca <sub>2</sub> Mn(III) <sub>2</sub> [Si <sub>4</sub> O <sub>13</sub> ](OH) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub>	[221a–b]
Akatoreite	H <sub>2</sub> Mn(II) <sub>9</sub> Al <sub>2</sub> [Si <sub>4</sub> O <sub>13</sub> ] <sub>2</sub> (OH) <sub>6</sub>	[222]
	Na <sub>4</sub> Sc <sub>2</sub> [Si <sub>4</sub> O <sub>13</sub> ]	[223]
	Rb <sub>2</sub> Si <sup>[6]</sup> [P <sub>4</sub> O <sub>13</sub> ]	[224]
	Ag <sub>10</sub> [Si <sub>4</sub> O <sub>13</sub> ]	[225]
	Ba <sub>2</sub> Nd <sub>2</sub> [Si <sub>4</sub> O <sub>13</sub> ]	[226]

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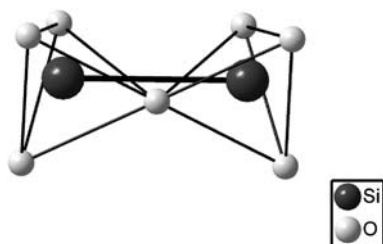
**Table 3** (continued)

Mineral name	Formula	Ref.
Medaite	Unbranched Pentasilicates $\{\infty\}^0 \text{ Pseudo-S}_3\text{Cl}_2$ $\text{Na}_4\text{Sn}_2[\text{Si}_5\text{O}_{16}](\text{H}_2\text{O})$	[227]
	Unbranched Hexasilicates $\{\infty\}^0 \text{ Pseudo-S}_4\text{Cl}_2$ $\text{HMn(II)}_6[\text{V(V)Si}_5\text{O}_{19}]$	[228]
	Open-branched Oligosilicates $\{\infty\}^0 \text{ Pseudo-Si}_2\text{Cl}_6$ $\text{In}_4[\text{Si}_2\text{P}_6\text{O}_{25}]$	[229]
	$\text{Si}_3^{[6]}[\text{Si}_2\text{P}_6\text{O}_{25}]$	[230]
	Mixed silicate-anion silicates $\{\infty\}^0 \text{ Pseudo-Ar} + \{\infty\}^0 \text{ Pseudo-Cl}_2$ $\text{Ca}_2\text{Al}_3[\text{SiO}_4][\text{Si}_2\text{O}_7]\text{O}(\text{OH})$	[231]
Zoisite	$\text{Ca}_2\text{Mn(III)}_3[\text{SiO}_4][\text{Si}_2\text{O}_7](\text{OH})_3$	[221b]
Macfallite	$\text{Mn(II)}_2\text{Al}_3[\text{SiO}_4][\text{Si}_2\text{O}_7]\text{O}(\text{OH})_3$	[232]
Sursassite	$(\text{Ca},\text{Mn})_2\text{Pb}_3[\text{SiO}_4][\text{Si}_2\text{O}_7]$	[233]
Ganomalite	$\text{Na}_2\text{Ca}_6[\text{SiO}_4][\text{Si}_2\text{O}_7]$	[234]
Vesuvianite	$\text{Ca}_{19}\text{Al}_{10}(\text{Mg},\text{Fe})_3[\text{SiO}_4][\text{Si}_2\text{O}_7]$	[235]
Orientite	$\{\infty\}^0 \text{ Pseudo-Ar} + \{\infty\}^0 \text{ Pseudo-SCl}_2$ $\text{Na}_4\text{Ca}_4[\text{SiO}_4][\text{Si}_3\text{O}_{10}]$	[236]
	$\text{Ca}_8\text{Mn(III)}_{10}[\text{SiO}_4]_3[\text{Si}_3\text{O}_{10}]_3(\text{OH})_{10}(\text{H}_2\text{O})_4$	[237]
	$\text{A}_4[\text{SiO}_4][\text{Si}_3\text{O}_{10}]$ with $\text{A} = \text{Ho}, \text{Tm}$	[238a,b]
	$\{\infty\}^0 \text{ Pseudo-Ar} + \{\infty\}^0 \text{ Pseudo-S}_2\text{Cl}_2$ $\text{Ag}_{18}[\text{SiO}_4]_2[\text{Si}_4\text{O}_{13}]$	[239]

### 5.2.1

#### Disilicates

This group of silicates is characterised by isolated  $[\text{Si}_2\text{O}_7]^{6-}$  anions. Each anion consists of two  $[\text{SiO}_4]$  tetrahedra joined by a common corner as seen in Fig. 3. Such anions are present in the ternary silicates  $\text{A}_6[\text{Si}_2\text{O}_7]$  ( $\text{A} = \text{Li}, \text{K}, \text{Rb}, \text{Cs}, \text{Ag}, \text{Tl}$ ), rankinite  $\text{Ca}_3[\text{Si}_2\text{O}_7]$ , in the mineral wadsleyite which is a high pressure phase of composition  $\text{Mg}_2\text{SiO}_4$  and in the HP phase of  $\text{Na}_2\text{Si}_3\text{O}_7$ , as well as in  $\text{In}_2[\text{Si}_2\text{O}_7]$  and  $\text{A(III)}_2[\text{Si}_2\text{O}_7]$  with  $\text{A(III)} = \text{Sc}, \text{Y}, \text{La}, \text{Ce}, \text{Pr}, \text{Nd}, \text{Sm}, \text{Eu}, \text{Gd}, \text{Ho}, \text{Er}, \text{Yb}$ . More than 60 quaternary disilicates have also been reported. The Si subarray is formed by  $(\text{Si} - \text{Si})^{6-}$  dimers which are isoelectronic with a halogen  $\text{X} - \text{X}$  molecule. This indicates that the Zintl–Klemm concept can be applied to them. Thus, if for example the six alkali metal atoms per formula unit would donate six electrons to the two silicon atoms, they would be converted into two  $\Psi\text{-Cl}$ , adopting the form of a  $\Psi\text{-Cl}_2$  molecule. In the latter, the two  $\Psi\text{-Cl}$  atoms are bonded by a single  $\sigma$ -bond



**Fig. 3** The structure of the disilicate anion  $[\text{Si}_2\text{O}_7]^{6-}$  in  $\text{K}_6[\text{Si}_2\text{O}_7]$ , consisting of two tetrahedra connected by a common corner. It can be considered as a  $\Psi\text{-Cl}_2$  molecule. The O atoms are docked close to the Cl–Cl bond and to the three lone pairs of each  $\Psi\text{-Cl}$  atom. The structure resembles that of the  $\text{Cl}_2\text{O}_7$  molecule

and the two octets are completed by three lone pairs on each Si atom, situated tetrahedrally with respect to the bond line. Now, if O atoms are located close to these lone pairs and also close to the midpoint of the bond line, we obtain the structure of the disilicate anion (see Fig. 3). It is worth mentioning that this anion has the same conformation as the molecule of  $\text{Cl}_2\text{O}_7$  [38].

An interesting example is that provided by the HP phase  $\text{Na}_2\text{Si}_3\text{O}_7$  [39]. This silicate can be written as  $\text{Na}_2\text{Si}^{[6]}\{\text{t}\}[\text{Si}_2^{[4]}\text{O}_7]$ . Its unit cell contains four formula units. An important characteristic of this compound is that it presents two kinds of coordination polyhedra for silicon. Four Si atoms per unit cell are hexa-coordinated and the eight remaining silicon atoms have tetrahedral coordination, forming four disilicate anions  $[\text{Si}_2\text{O}_7]^{6-}$ . To account for this geometry, one has to assume that each tetrahedrally coordinated Si atom has received  $3\text{ e}^-$  (a total of  $24\text{ e}^-$ ) transforming it into  $\Psi\text{-Cl}$  and every two of them mimicking the structure of a  $\text{Cl}_2$  molecule. These  $24\text{ e}^-$  are provided by the eight Na atoms ( $8\text{ e}^-$ ) and by the four hexa-coordinated Si atoms ( $16\text{ e}^-$ ). This indicates that the Si atoms have an amphoteric character which seems to be induced by the application of pressure. It should be mentioned that this phenomenon was also observed in the structures of aluminates [8] in which the basicity can be identified with the octahedral coordination (as in silicon) whereas the acceptor character leads to the formation of Zintl polyanions and hence to the tetrahedral coordination.

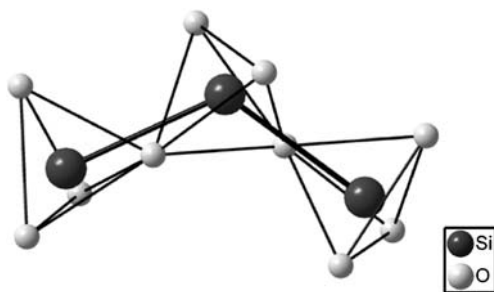
### 5.2.2

#### Other Oligosilicates

In this section, we will discuss some compounds which contain small, discrete, unbranched or branched, groups of  $n$   $[\text{TO}_4]$  tetrahedra, as listed in Table 3.

$\text{Na}_4\text{Cd}_2[\text{Si}_3\text{O}_{10}]$  [40] contains groups of three tetrahedra forming discrete anions  $[\text{Si}_3\text{O}_{10}]^{8-}$  which are represented in Fig. 4. The T atom skeleton is



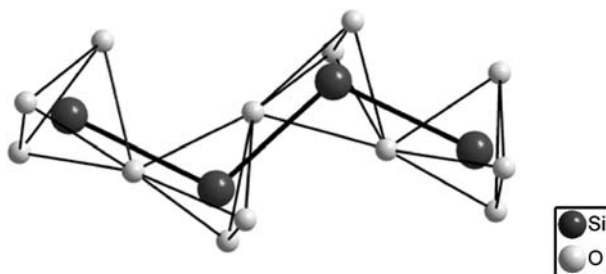


**Fig. 4** The structure of the oligosilicate anion  $[\text{Si}_3\text{O}_{10}]^{8-}$  in  $\text{Na}_4\text{Cd}_2[\text{Si}_3\text{O}_{10}]$  consists of three tetrahedra connected by common corners. Its Si subarray adopts the same structure as the  $\text{SCL}_2$  molecule

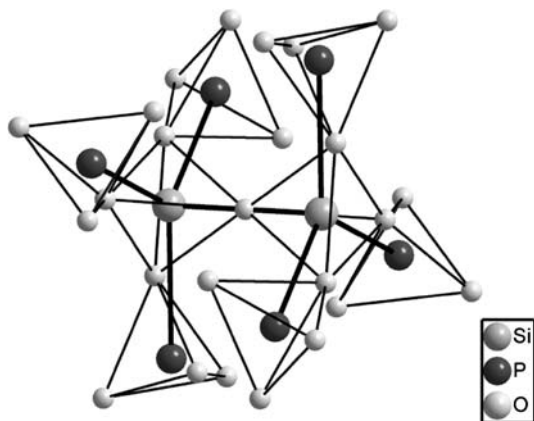
not linear, the Si – Si – Si angle being  $114.33^\circ$ . This structure can be understood in the light of the Zintl–Klemm concept. The Na and Cd atoms can donate  $8\text{ e}^-$  per formula unit to the Si atoms. The central one is converted into  $\Psi\text{-S}$  and the two terminal ones are converted into  $\psi\text{-Cl}$ . The final pseudo-stoichiometry would be  $\Psi\text{-SCL}_2$ . The real  $\text{SCL}_2$  molecule is similar in geometry although with a lower Cl – S – Cl angle of  $102.48^\circ$ .

In  $\text{Ag}_{10}[\text{Si}_4\text{O}_{13}]$  [41], every four  $[\text{TO}_4]$  tetrahedra are linearly connected as represented in Fig. 5. This oligosilicate anion can also be explained by the Zintl–Klemm concept. The  $10\text{ e}^-$  per formula unit provided by the Ag atoms convert the two central Si atoms into  $\Psi\text{-S}$  and the two terminal ones into  $\Psi\text{-Cl}$ , giving rise to a pseudo-anion of stoichiometry  $\Psi\text{-S}_2\text{Cl}_2$ . The geometry is similar to that of the Zintl polyanion found in  $\text{Ba}_3\text{P}_4$  (also with  $\Psi\text{-S}_2\text{Cl}_2$  stoichiometry) [42]. A similar T atom subarray exists in the aluminate  $\text{Na}_{14}[\text{Al}_4\text{O}_{13}]$  [8].

As an example of a branched oligosilicate the structure of  $\text{In}_4[\text{Si}_2\text{P}_6\text{O}_{25}]$  [43] will be discussed. This silicophosphate anion has an interesting



**Fig. 5** The oligosilicate anion  $[\text{Si}_4\text{O}_{13}]^{10-}$  in  $\text{Ag}_{10}[\text{Si}_4\text{O}_{13}]$  is formed by four  $[\text{SiO}_4]$  tetrahedra which are connected by common corners. The Si subarray contains groups of four Si atoms resembling the Zintl polyanion  $[\text{P}_4]^{6-}$  in the Zintl phase  $\text{Ba}_3\text{P}_4$



**Fig. 6** The structure of the anion  $[\text{Si}_2\text{P}_6\text{O}_{25}]^{12-}$  existing in  $\text{In}_4[\text{Si}_2\text{P}_6\text{O}_{25}]$ . The two central Si atoms remain as silicon atoms adopting a four-fold connectivity. The P atoms are converted into mono-connected  $\Psi$ -halogen. The resulting stoichiometry is  $\Psi\text{-Si}_2\text{Cl}_6$ . The structure resembles that of the Zintl polyanion  $[\text{Sn}_2\text{P}_6]^{12-}$  in the Zintl phase  $\text{Ba}_6\text{Sn}_2\text{P}_6$  and also that of the  $\text{Si}_2\text{I}_6$  molecule

structure which is represented in Fig. 6. It is formed by two Si-centred tetrahedra per formula unit which share one corner. Each of these tetrahedra are further linked, by common corners, to three P-centred tetrahedra. Looking at the Si – P subarray, it can be seen that its structure is similar to that of a  $\text{C}_2\text{H}_6$  molecule. If we apply the Zintl–Klemm concept we see that the 12 electrons per formula unit provided by the In atoms can serve to convert the 6 P atoms into  $\Psi\text{-Cl}$  in such a way that the final stoichiometry is  $\Psi\text{-Si}_2\text{Cl}_6$  and this is just the conformation of the similar  $\text{Si}_2\text{I}_6$  molecule. The T-atom subarray is also similar to the  $[\text{Sn}_2\text{P}_6]^{12-}$  polyanion in the Zintl phase  $\text{Ba}_6\text{Sn}_2\text{P}_6$  [44]. The same T-atom subarray also exists in  $\text{Si}_3^{[6]}[\text{Si}_2^{[4]}\text{P}_6\text{O}_{25}]$  [45], a compound in which, again, silicon has an amphoteric character by which the donor Si atoms are octahedrally coordinated whereas the acceptor Si atoms are tetrahedrally coordinated forming part of the tetrahedral anions.

### 5.3

#### Ring Silicates

A list of ring silicates is given in Table 4.

#### 5.3.1

##### Single-Ring Silicates

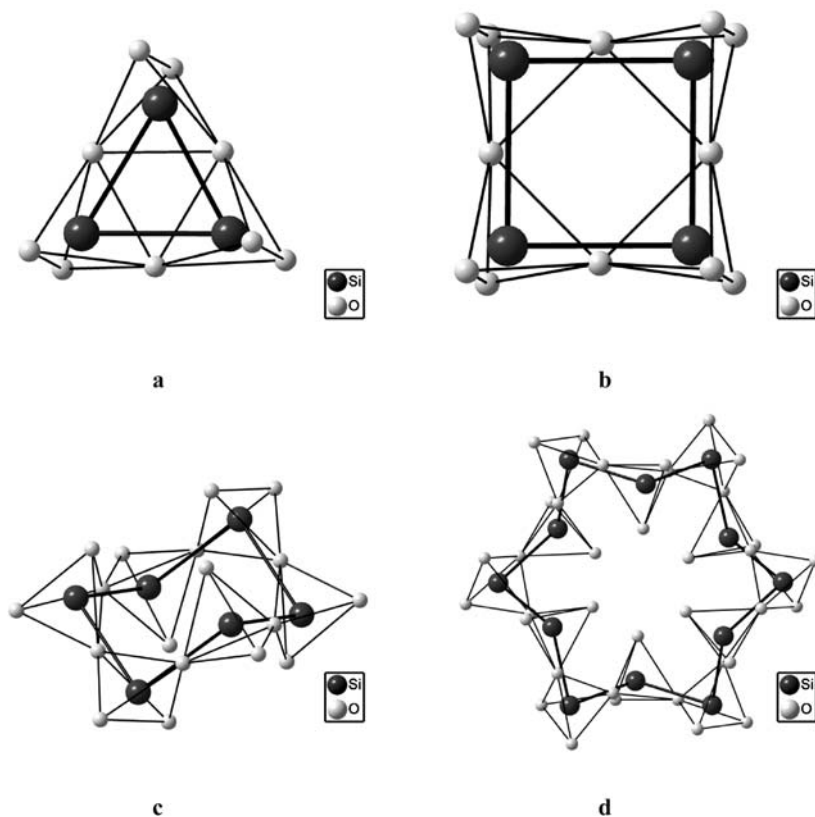
The compounds which will be discussed next have in common the existence of isolated rings of condensed  $[\text{SiO}_4]$  groups which share two corners each

**Table 4**

Mineral name	Formula	Ring silicates		
		Single-ring silicates {1r} Pseudo- $S_m$		
		$P^R$	$m$	Ref.
Pseudowollastonite Ca-catapleite	$A_6[Si_3O_9]$ with $A = K, Rb, Cs$	3	3	[240]
	$A_2Be_2[Si_3O_9]$ with $A = Na, K$	3	3	[241a–b]
	$A_3[Si_3O_9]$ with $A = \underline{Ca}, Sr$	3	3	[242a–b]
	$CaZr[Si_3O_9](H_2O)_2$	3	3	[243]
Benitoite, bazirite pabstite	$Ca_3Y_2[Si_3O_9]_2$	3	3	[244]
	$BaA[Si_3O_9]$ with $A = Si, \underline{Ti}, \underline{Zr}, \underline{Sn}$	3	3	[245]
	$La_3[Si_3O_9]F_3$	3	3	[246]
Papagoite	$H_4K_4[Si_4O_{12}]$	4	4	[247]
	$A_8[Si_4O_{12}]Cl_8$ with $A = Ca, Eu(II)$	4	4	[248a–b]
	$Ca_2Cu_2Al_2[Si_4O_{12}](OH)_6$	4	4	[249]
	$Ca_2Zr[Si_4O_{12}]$	4	4	[250]
	$Sr_4[Si_4O_{12}]$	4	4	[251]
	$Ba_2Cu_2[Si_4O_{12}]$	4	4	[252]
	$Ba_2V_2[Si_4O_{12}]O_2$	4	4	[253]
	$Na_4Ca_4[Si_6O_{18}]$	6	6	[254]
	$Na_6Sr_3[Si_6O_{18}]$	6	6	[255]
	$Na_8Si^{[6]}[Si_6O_{18}]$	6	6	[256]
Petarasite	$Na_5Zr_2[Si_6O_{18}]_2Cl(H_2O)$	6	6	[257]
Beryl	$Be_3Al_2[Si_6O_{18}]$	6	6	[258]
Scawtite	$Ca_7[Si_6O_{18}](CO_3)(H_2O)_2$	6	6	[259]
Diopside	$Cu_6[Si_6O_{18}](H_2O)_6$	6	6	[260]
Muirite	$Ca_2Ba_{10}Ti_2[Si_8O_{24}](OH, Cl)_{16}$	8	8	[261]
Megacyclite	$Na_6Si^{[6]}[Si_9O_{27}]$	9	9	[262]
	$A(I)_{15}A(III)_3[Si_{12}O_{36}]$ with $A(I) = Na, Ag$ $A(III) = Sc, Y, REE$	12	12	[263]
	$A(I)_{16}A(II)_4[Si_{12}O_{36}]$ with $A(I) = Na, K$ $A(II) = Ca, Sr$	12	12	[264]
	$H_{18}Na_{16}K_2[Si_{18}O_{54}](H_2O)_{38}$	18	18	[265]
	Double-ring silicates {uB, 2r} Pseudo- $P_m$			
	$Na_3Y[Si_6O_{15}]$	3	6	[266]
Moskvinitite	$Na_2K(Y, REE)[Si_6O_{15}]$	3	6	[267]
Turkestanite, steacyite, arapovite	$K_{1-x}(Ca, Na)_2A(IV)[Si_8O_{20}](H_2O)_n$ with $A = Th, U$	4	8	[268a–c]
Milarite	$KBe_2Ca_2Al[Si_{12}O_{30}](H_2O)_{1-x}$	6	12	[269]
Osumilite	$(Na, K)(Fe, Mg)_2(Al, Fe)_3[(Al, Si)_{12}O_{30}]$	6	12	[270]

with two adjacent tetrahedra. They are grouped according to the number of tetrahedra forming a ring (ring periodicity  $P^R = 3, 4, 6, 8, 9, 12, 18$ ).

Following the Zintl–Klemm concept, the electropositive cations provide two electrons to each Si atom converting them into  $\Psi$ -S. An example of this is the mineral pabstite  $\text{BaSn}[\text{Si}_3\text{O}_9]$  [46] in which isolated cyclic  $[\text{Si}_3\text{O}_9]^{6-}$  anions exist. This can be interpreted as if the Ba and Sn atoms would donate  $6\text{ e}^-$  to the three Si atoms, converting them into pseudo-S ( $\Psi$ - $\text{S}_3$  molecule). Thus, in these kinds of compounds, the Si atoms adopt the structures of several different molecules observed in elemental sulfur, that is, the triangular  $\text{S}_3$  molecules observed in sulfur vapour [47], the square  $\text{S}_4$  molecule, also observed in the gas phase [48], the chair-conformed  $\text{S}_6$  rings and the puckered  $\text{S}_8$  rings existing in crystalline sulfur [49, 50], and the  $\text{S}_{12}$  molecules, also stable in the solid state [51]. Several such polyanions are represented in Fig. 7. If the O atoms are located close to the two lone pairs and also in the vicinity of the midpoints of the two hypothetical Si – Si bonds, the tetrahedral coordina-



**Fig. 7** The structures of the ring silicate anions  $[\text{Si}_3\text{O}_9]^{6-}$  (a),  $[\text{Si}_4\text{O}_{12}]^{8-}$  (b),  $[\text{Si}_6\text{O}_{18}]^{12-}$  (c) and  $[\text{Si}_{12}\text{O}_{36}]^{24-}$  (d), found in the compounds  $\text{K}_6[\text{Si}_3\text{O}_9]$ ,  $\text{Sr}_4[\text{Si}_4\text{O}_{12}]$ ,  $\text{Na}_4\text{Ca}_4[\text{Si}_6\text{O}_{18}]$  and  $\text{Na}_{15}\text{Sc}_3[\text{Si}_{12}\text{O}_{36}]$  respectively. In all of them, the Si atoms behave as pseudo-S adopting the structures of cyclic  $\text{S}_3$ ,  $\text{S}_4$ ,  $\text{S}_6$  and  $\text{S}_{12}$  molecules respectively

tion of silicon is obtained. These hypothetical Si – Si bonds are also drawn in Fig. 7.

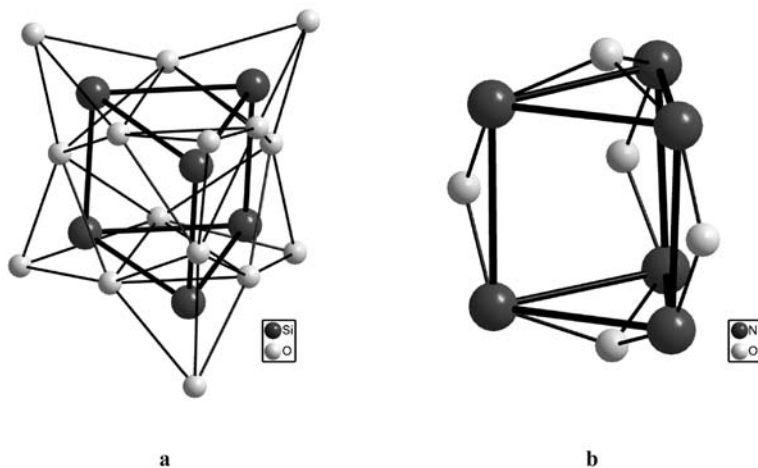
A special case is the HP phase (2 GPa) of  $\text{K}_2\text{Si}_4\text{O}_9$  [52]. According to the crystal chemical formula  $\text{K}_2\text{Si}^{[6]} \{uB, 3, 1r\}[\text{Si}_3\text{O}_9]$ , its structure contains two types of coordination polyhedra around silicon, i.e. octahedra and tetrahedra. The latter form three-membered rings. It can be interpreted under the assumption that the two K atoms and the hexa-coordinated Si atom, per formula unit, would donate their valence electrons to the three tetra-coordinated Si atoms. Thus, the HP polymorph of  $\text{K}_2\text{Si}_4\text{O}_9$  shows a skeleton in which the T atoms are converted into  $\Psi$ -S ions forming isolated  $\Psi$ - $\text{S}_3$  molecules.

A similar amphoteric behaviour of the Si atoms is found in the silicates  $\text{Na}_8\text{Si}^{[6]} \{uB, 1r\} [\text{Si}_6^{[4]} \text{O}_{18}]$  [53] and  $\text{Na}_6\text{Si}_3^{[6]} \{uB, 1r\} [\text{Si}_9^{[4]} \text{O}_{27}]$  [54].

### 5.3.2

#### Double-Ring Silicates

This group of compounds contains pairs of rings connected with each other. One of these compounds is  $\text{Na}_3\text{Y} \{uB, 2r\} [\text{Si}_6\text{O}_{15}]$  [55]. The structure of its silicate anion is represented in Fig. 8a and is formed by two *dreier* rings which connect further to form isolated trigonal prisms of Si atoms and is also consistent with the Zintl–Klemm concept. Considering that the Na and Y atoms donate  $6 e^-$  per formula unit to the six Si atoms, these are converted into  $\Psi$ -P

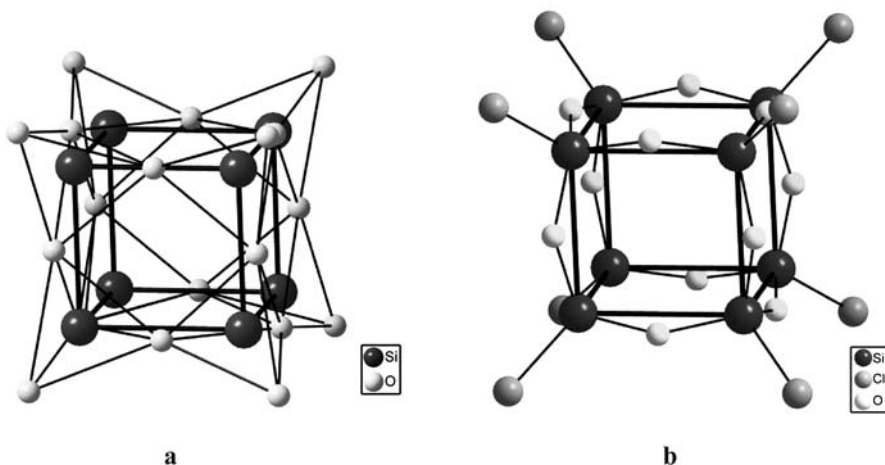


**Fig. 8** **a** The structure of the double ring  $[\text{Si}_6\text{O}_{15}]^{6-}$  anion existing in  $\text{Na}_3\text{Y} \{uB, 2r\} [\text{Si}_6\text{O}_{15}]$ . The Si atoms show a 3-fold connectivity typical of a  $\Psi$ -P atom. The Si atoms form a trigonal prism similar to that formed by the N atoms in  $\text{N}_6\text{S}_5$  **b** and also similar to the structure of the isoelectronic  $\text{Si}_6\text{H}_6$  (prismane-like)

atoms which adopt a threefold connectivity, just that occurring in a trigonal prism. Once more, the O atoms are situated close to both, the midpoints of the hypothetical Si – Si bonds and the lone pairs of each  $\Psi$ -P atom. This gives rise to the polyanion  $[\text{Si}_6\text{O}_{15}]^{6-}$  which is represented in Fig. 8a.

Although none of the P allotropes has this type of structure, the connectivity is characteristic of a Group 15 element and a similar skeleton is formed by the N atoms in the binary compound  $\text{N}_6\text{S}_5$  [56] which is represented in Fig. 8b. The differences between both compounds refer only to the amount of anions (O and S, respectively) added to the  $\text{Si}_6$  and  $\text{N}_6$  skeleton, respectively. Thus, in the oxosilicate, all the bonding and lone pairs of the  $\Psi$ -P atoms are captured by oxygen atoms whereas in the sulfide  $\text{N}_6\text{S}_5$ , three S atoms are located close to the lateral edges of the prism and two additional sulfur atoms are capping the two triangular bases. It should also be mentioned that the iso-electronic  $\text{Si}_6\text{H}_6$  molecule (prismane-like) could be a stable species as derived from theoretical calculations [57].

Another example of this kind of compounds is provided by turkestanite  $\text{K}_{<1}(\text{Na}, \text{Ca})_2\text{Th} \{uB, 4, 2r\}[\text{Si}_8\text{O}_{20}]$  [13] mentioned in Sect. 2. It contains *vierer* double rings in which the Si atoms form an isolated cube, as seen in Fig. 9a. The electron transfer in this compound is also compatible with the Zintl–Klemm concept. The electropositive atoms (K, Na, Ca and Th) provide eight  $e^-$  per formula unit which convert the eight Si atoms into  $\Psi$ -P atoms with a threefold connectivity, typical of the Group 15 elements. Thus, the Si atoms ( $\Psi$ -P atoms) would form three hypothetical two-centre, two-electron



**Fig. 9** **a** The structure of the double ring  $[\text{Si}_8\text{O}_{20}]^{8-}$  anion existing in turkestanite  $\text{K}_{1-x}(\text{Ca}, \text{Na})\text{Th}\{uB, 2r\}[\text{Si}_8\text{O}_{20}]$ . The Si atoms show a connectivity typical of a  $\Psi$ -P atom, forming a cube in which the O atoms are located close to both the midpoints of the Si – Si bonds and the lone pair regions. The structure is similar to that of the isoelectronic  $\text{Si}_8\text{O}_{12}\text{Cl}_8$  molecule shown in **(b)**

Si–Si bonds. The O atoms are then docked close to the midpoints of the edges of the  $[\text{Si}_8]$  cubes and also close to the lone pairs of the  $\Psi$ -P atoms. This type of structure has not been observed in any of the elements of Group 15 of the PSE but it could be a plausible structure for both, the elements and the oxides derived from them. In fact, a similar cage of formula  $\text{P}_4\text{Si}_4\text{R}_4$  ( $\text{R} = \text{t-But}$ ) has been isolated [58] in which the  $\text{P}_4\text{Si}_4$  distorted cubes are isoelectronic with the hypothetical  $\text{P}_8$  molecule if we consider that the two electrons of the Si–C bonds are equivalent to lone pairs on the P atoms. Theoretical studies carried out on the cubane analogues of Si also show the stability of the  $\text{Si}_8\text{H}_8$  molecule, isoelectronic with the  $\text{P}_8$  molecule [57]. In connection with this it is also interesting to mention the existence of the compound  $\text{Si}_8\text{O}_{12}\text{Cl}_8$  ( $\text{Si}_8\text{X}_{20}$ ) [59], even though it is neither a silicate nor a binary oxide. The structure of this silicon oxychloride is represented in Fig. 9b. Here, the Si atoms also form *vierer* double rings (cubes) and the O atoms are situated close to the midpoints of the hypothetical Si–Si bonds, just at the points where  $2e^-$  are involved in the bonds. The remaining unpaired electron would occupy an empty hybrid orbital, just in the position occupied by the monovalent Cl atoms.

## 5.4

### Chain Silicates

In Table 5, chain silicates are compiled. They are arranged according to their chain multiplicity into single-, double-, triple-, quadruple- and quintuple-chain silicates. Within each of these groups they are arranged with regard to branchedness (unbranched, open-branched and loop-branched), and further according to their chain periodicity  $P^C$  (see paragraphs on formula notation in Sect. 2).

#### 5.4.1

##### Single-Chain Silicates

In the vast number of silicates which contain unbranched single chains, each condensated  $[\text{SiO}_4]$  tetrahedron shares two of its four O atoms with two adjacent tetrahedra. This implies that the infinite chains contain only two-connected tetrahedra. Following the Zintl–Klemm concept, the electropositive cations, which in the given formulas precede the silicate anion, donate two electrons to each of the Si atoms converting them into  $\Psi$ -S and giving rise to a twofold connectivity. If the O atoms are located close to the midpoint of each Si–Si bond and also to the two electron lone pairs of each Si atom, a tetrahedral coordination around the Si atoms is formed. The topology of the skeleton of  $\Psi$ -S atoms is the same as that of elemental fibrous sulfur. The chain observed in the silicate  $\text{Na}_4[\text{Si}_2\text{O}_6]$  [60] is represented in Fig. 10. The Si-chains of the skeleton are identical to those found in some Zintl phases such

Table 5

Chain silicates						
Single-chain silicates						
Unbranched single-chain silicates						
{ <i>uB</i> , 1 <sup>1</sup> <sub>∞</sub> } Pseudo-Si <sub>k</sub> P <sub>l</sub> S <sub>m</sub> Cl <sub>n</sub>						
Mineral name	Formula	<i>p</i> <sup>C</sup>	<i>k</i>	<i>l</i>	<i>m</i>	<i>n</i> Ref.
	Cu[SiO <sub>3</sub> ]	1	0	0	1	0 [271]
	A <sub>4</sub> [Si <sub>2</sub> O <sub>6</sub> ] with A = Li, Na, Ag	2	0	0	2	0 [272a–c]
	Ba <sub>2</sub> [Si <sub>2</sub> O <sub>6</sub> ]	2	0	0	2	0 [273]
	Li <sub>2</sub> (Mg, Cu)Cu <sub>2</sub> [Si <sub>2</sub> O <sub>6</sub> ] <sub>2</sub>	2	0	0	2	0 [274]
Ramsayite	Na <sub>2</sub> Ti <sub>2</sub> [Si <sub>2</sub> O <sub>6</sub> ] <sub>2</sub> O <sub>3</sub>	2	0	0	2	0 [275]
Clinopyroxenes, e.g. spodumene, jadeite, aegirine, diopside, hedenbergite	A A'[Si <sub>2</sub> O <sub>6</sub> ] with A = Li, Na, Mg, Ca, Mn, Fe(II), Zn; A' = Mg, Ca, Al, Ga, Sc, V, Fe(III)	2	0	0	2	0
Orthopyroxenes, e.g. enstatite, ferrosilite	MgA[Si <sub>2</sub> O <sub>6</sub> ] with A = <u>Mg</u> , Mn, <u>Fe(II)</u>	2	0	0	2	0
Pectolite	HNaCa <sub>2</sub> [Si <sub>3</sub> O <sub>9</sub> ]	3	0	0	3	0 [276]
Wollastonite, parawollastonite	Ca <sub>3</sub> [Si <sub>3</sub> O <sub>9</sub> ]	3	0	0	3	0 [277a–b]
Sørensenite	Na <sub>4</sub> Be <sub>2</sub> Sn[Si <sub>3</sub> O <sub>9</sub> ] <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub>	3	0	0	3	0 [278]
Batisite	Na <sub>2</sub> BaTi <sub>2</sub> [Si <sub>4</sub> O <sub>12</sub> ] <sub>2</sub> O <sub>2</sub>	4	0	0	4	0 [279]
Haradaite, suzukiite	A <sub>2</sub> V(IV) <sub>2</sub> [Si <sub>4</sub> O <sub>12</sub> ] <sub>2</sub> O <sub>2</sub> with A = Sr, Ba	4	0	0	4	0 [280a–b]
Rhodonite	(Mn, Ca, Mg, Fe) <sub>5</sub> [Si <sub>5</sub> O <sub>15</sub> ]	5	0	0	5	0 [281]
Santaclaraite	HCaMn <sub>4</sub> [Si <sub>5</sub> O <sub>15</sub> ](OH)(H <sub>2</sub> O)	5	0	0	5	0 [282]
Gaidonnayite	Na <sub>4</sub> Zr <sub>2</sub> [Si <sub>6</sub> O <sub>18</sub> ](H <sub>2</sub> O) <sub>4</sub>	6	0	0	6	0 [283]
Penkvilksite	Na <sub>4</sub> Ti <sub>2</sub> [Si <sub>6</sub> O <sub>18</sub> ](H <sub>2</sub> O) <sub>4</sub>	6	0	0	6	0 [284]
	K <sub>4</sub> A <sub>2</sub> [Si <sub>6</sub> O <sub>18</sub> ] with A = Ti, Sn	6	0	0	6	0 [285]
Pyroxmangite	Mn <sub>7</sub> [Si <sub>7</sub> O <sub>21</sub> ]	7	0	0	7	0 [286]
(Ferrosilite III)	Fe <sub>9</sub> [Si <sub>9</sub> O <sub>27</sub> ]	9	0	0	9	0 [287]
	Cs <sub>6</sub> Sb <sub>6</sub> [Si <sub>12</sub> O <sub>36</sub> ] <sub>2</sub> O <sub>6</sub>	12	0	0	12	0 [288]
Alamosite	Pb <sub>12</sub> [Si <sub>12</sub> O <sub>36</sub> ]	12	0	0	12	0 [289]
	Na <sub>24</sub> Y <sub>8</sub> [Si <sub>24</sub> O <sub>72</sub> ]	24	0	0	24	0 [290]
Open-branched single-chain silicates						
{ <i>oB</i> , 1 <sup>1</sup> <sub>∞</sub> } Pseudo-Si <sub>k</sub> P <sub>l</sub> S <sub>m</sub> Cl <sub>n</sub>						
Astrophyllite	NaK <sub>2</sub> Mg <sub>2</sub> (Fe, Mn) <sub>5</sub> Ti <sub>2</sub> [Si <sub>4</sub> O <sub>12</sub> ] <sub>2</sub> (O, OH, F) <sub>7</sub>	2	0	2	0	2 [291]
	Eu <sub>2</sub> [Si <sup>[1;4]</sup> <sub>1</sub> P <sup>[1;2]</sup> <sub>2</sub> P <sup>[1;1]</sup> <sub>2</sub> O <sub>15</sub> ]	3	1	0	2	2 [292]
Aenigmatite	Na <sub>2</sub> A <sub>6</sub> [Si <sub>6</sub> O <sub>18</sub> ](O, OH) <sub>2</sub> with A = Mg, (Mg, Fe), (Fe, Ti)	4	0	2	2	2 [293a–c]
Saneroite	HNa <sub>2–x</sub> Mn <sub>5</sub> [Si <sub>5</sub> (Si, V)O <sub>18</sub> ](OH) <sub>2</sub>	5	0	1	4	1 [294]
Loop-branched single-chain silicates						
{ <i>lB</i> , 1 <sup>1</sup> <sub>∞</sub> } Pseudo-Si <sub>k</sub> P <sub>l</sub> S <sub>m</sub> Cl <sub>n</sub>						
	Li <sub>2</sub> Mg <sub>2</sub> [Si <sub>4</sub> O <sub>11</sub> ]	3	0	2	2	0 [295]

continued on next page



**Table 5** (continued)

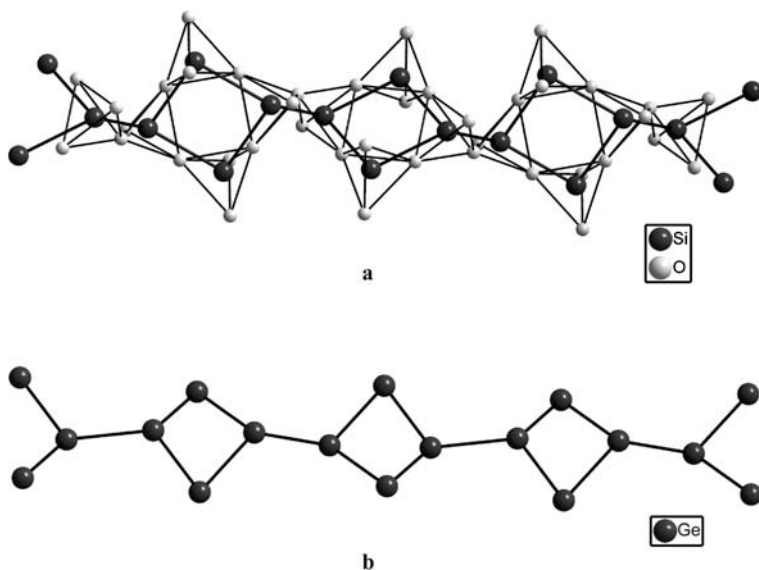
Mineral name	Formula	$p^C$	$k$	$l$	$m$	$n$	Ref.
Stillwellite	REE[B <sup>[4]</sup> Si <sup>[1;2]</sup> O <sub>5</sub> ]	3	1	0	1	0	[296]
	CaBa <sub>3</sub> Cu[Si <sub>6</sub> O <sub>17</sub> ]	4	0	2	4	0	[297]
Deerite	Fe(II) <sub>6</sub> Fe(III) <sub>3</sub> [Si <sub>6</sub> O <sub>17</sub> ](OH) <sub>5</sub> O <sub>3</sub>	4	0	2	4	0	[298]
	V[Si <sup>[1;4]</sup> P <sup>[1;2]</sup> O <sub>8</sub> ]O	4	1	0	2	0	[299]
Vlasovite	Na <sub>4</sub> Zr[Si <sub>8</sub> O <sub>22</sub> ]	6	0	4	4	0	[300]
Pellyite	Ca <sub>2</sub> Ba <sub>4</sub> (Mg, Fe)[Si <sub>8</sub> O <sub>22</sub> ]	8	0	4	4	0	[301]
Liebauite	Ca <sub>6</sub> Cu <sub>10</sub> [Si <sub>18</sub> O <sub>52</sub> ]	14	0	4	14	0	[302]
Double-chain silicates							
Unbranched double-chain silicates							
	{ <b>uB</b> , 2 <sup>1</sup> <sub>∞</sub> } Pseudo-Si <sub>k</sub> P <sub>l</sub> S <sub>m</sub> Cl <sub>n</sub>						
	H <sub>2</sub> Cs <sub>2</sub> [Si <sub>4</sub> O <sub>10</sub> ]	2	0	4	0	0	[303]
	Na <sub>2</sub> A <sub>2</sub> [Si <sub>4</sub> O <sub>10</sub> ] with A = Rb, Cs	2	0	4	0	0	[304]
Amphiboles, e.g. tremolite, cumming- tonite, hornblendes	A <sub>1-x</sub> A' <sub>2</sub> A'' <sub>5</sub> [(Al, Si) <sub>4</sub> O <sub>11</sub> ] <sub>2</sub> (OH, F) <sub>2</sub> with A = Na, K; A' = Li, Na, Mg, Ca, Mn, Fe(II); A'' = Mg, Mn, Fe(II), Fe(III), Al, Ti	2	0	2	2	0	
Sillimanite	Al <sub>2</sub> <sup>[6]</sup> [Al <sub>2</sub> Si <sub>2</sub> O <sub>10</sub> ]	2	0	4	0	0	[305]
Tobermorite	Ca <sub>5</sub> [Si <sub>6</sub> O <sub>17</sub> ](H <sub>2</sub> O) <sub>5</sub>	3	0	2	4	0	[306]
Xonotlite	Ca <sub>6</sub> [Si <sub>6</sub> O <sub>17</sub> ](OH) <sub>2</sub>	3	0	2	4	0	[307]
Epididymite	Na <sub>2</sub> Be <sub>2</sub> [Si <sub>6</sub> O <sub>15</sub> ](H <sub>2</sub> O)	3	0	6	0	0	[308]
Narsarsukite	Na <sub>4</sub> Ti <sub>2</sub> [Si <sub>8</sub> O <sub>20</sub> ]O <sub>2</sub>	4	0	8	0	0	[309]
Inesite	Ca <sub>2</sub> Mn <sub>7</sub> [Si <sub>10</sub> O <sub>28</sub> ](OH) <sub>2</sub> (H <sub>2</sub> O) <sub>5</sub>	5	0	4	6	0	[310]
Emeleusite, zektzerite, tuhualite	A <sub>2</sub> A' <sub>2</sub> 'A'' <sub>2</sub> '''[Si <sub>12</sub> O <sub>30</sub> ] with A = <u>Li</u> , <u>Na</u> , Mg, <u>Fe(II)</u> ; A' <sub>2</sub> = Na; A'' <sub>2</sub> = Na; A''' <sub>2</sub> = Mg, Fe(III), Y, Zr	6	0	12	0	0	[311a–f]
Loop-branched double-chain silicates							
	{ <b>lB</b> , 2 <sup>1</sup> <sub>∞</sub> } Pseudo-Si <sub>k</sub> P <sub>l</sub> S <sub>m</sub> Cl <sub>n</sub>						
Litidionite	Na <sub>2</sub> K <sub>2</sub> Cu <sub>2</sub> [Si <sub>8</sub> O <sub>20</sub> ]	3	0	8	0	0	[312]
	Li <sub>4</sub> Ca <sub>4</sub> [Si <sub>10</sub> O <sub>26</sub> ]	3	0	8	2	0	[313]
Tinaksite	HNaK <sub>2</sub> Ca <sub>2</sub> Ti[Si <sub>7</sub> O <sub>19</sub> ]O	3	0	4	3	0	[314]
Unbranched triple-chain silicates							
	{ <b>uB</b> , 3 <sup>1</sup> <sub>∞</sub> } Pseudo-Si <sub>k</sub> P <sub>l</sub> S <sub>m</sub> Cl <sub>n</sub>						
	Na <sub>2</sub> Mg <sub>4</sub> [Si <sub>6</sub> O <sub>16</sub> ](OH) <sub>2</sub>	2	0	4	2	0	[315]
Jimthompsonite	(Mg, Fe) <sub>5</sub> [Si <sub>6</sub> O <sub>16</sub> ](OH) <sub>2</sub>	2	0	4	2	0	[316]
	Ba <sub>4</sub> [Si <sub>6</sub> O <sub>16</sub> ]	2	0	4	2	0	[317]
Unbranched quadruple-chain silicates							
	{ <b>uB</b> , 4 <sup>1</sup> <sub>∞</sub> } Pseudo-Si <sub>k</sub> P <sub>l</sub> S <sub>m</sub> Cl <sub>n</sub>						
	Ba <sub>5</sub> [Si <sub>8</sub> O <sub>21</sub> ]	2	0	6	2	0	[317]
Frankamenite	Na <sub>3</sub> K <sub>3</sub> Ca <sub>5</sub> [Si <sub>12</sub> O <sub>30</sub> ](OH, F)(H <sub>2</sub> O)	3	0	12	0	0	[318]
	K <sub>8</sub> Cu <sub>4</sub> [Si <sub>16</sub> O <sub>40</sub> ]	4	0	16	0	0	[319]
Unbranched quintuple-chain silicates							
	{ <b>uB</b> , 5 <sup>1</sup> <sub>∞</sub> } Pseudo-Si <sub>k</sub> P <sub>l</sub> S <sub>m</sub> Cl <sub>n</sub>						
	Ba <sub>6</sub> [Si <sub>10</sub> O <sub>26</sub> ]	2	0	8	2	0	[317]



**Fig. 10** The structure of an unbranched single chain anion existing in  $\text{Na}_4\{\text{uB}, 2, 1_\infty^1\} [\text{Si}_2\text{O}_6]$ , to show its similarity with the chains of fibrous sulfur and with the asbestos-like  $\text{SO}_3$  oxide

as BaSi [61] where the Si atoms can also be regarded as  $\Psi$ -S. In fact, the BaSi substructure, in the HT phase of  $\text{Ba}_2[\text{Si}_2\text{O}_6]$  [62], is almost identical to the structure of BaSi itself, so that  $\text{Ba}_2[\text{Si}_2\text{O}_6]$  is an example of the so-called *real stuffed alloys* [63].

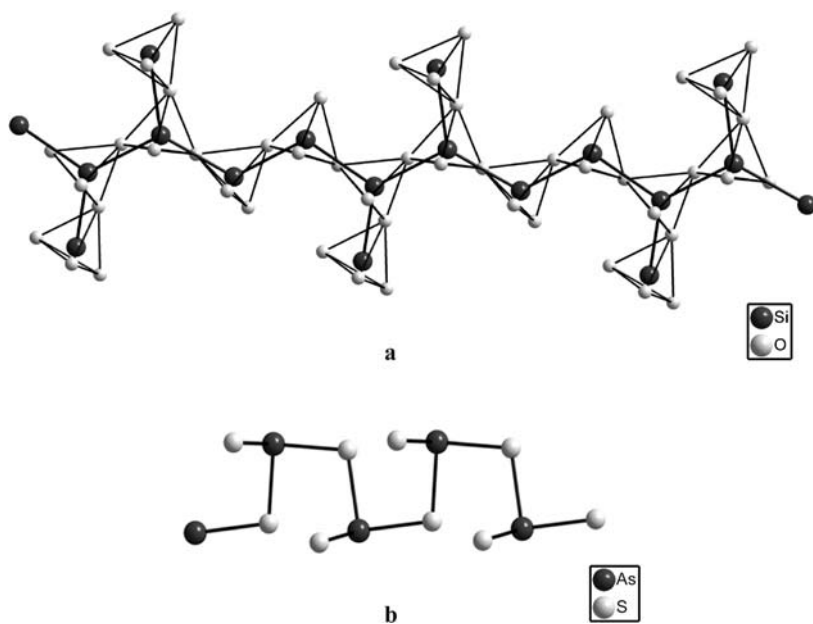
The structure of the loop-branched single chain observed in vlasovite  $\text{Na}_4\text{Zr}_2\{\text{IB}, 6, 1_\infty^1\} [\text{Si}_8\text{O}_{22}]$  [64] is presented in Fig. 11a. Sodium and zirconium atoms transfer 12 electrons per formula unit to the eight silicon atoms, transforming four of them into  $\Psi$ -P and four into  $\Psi$ -S. The resulting pseudo-stoichiometry is  $\Psi$ -PS. This kind of chain is also observed in the room-temperature polymorph of the Zintl phase  $\text{Ba}_3\text{Ge}_4$  [65]. In this compound, the



**Fig. 11** **a** View of the loop-branched single chain in vlasovite  $\text{Na}_4\text{Zr}_2\{\text{IB}, 6, 1_\infty^1\} [\text{Si}_8\text{O}_{22}]$ . The chain is composed of  $\Psi$ -P and  $\Psi$ -S pseudo-atoms in the ratio 1 : 1. **b** The same type of chain is formed by the Ge atoms in the Zintl phase  $\text{Ba}_3\text{Ge}_4$

three Ba atoms donate six electrons per formula unit to the Ge atoms converting two of them into  $\Psi$ -As and the other two into  $\Psi$ -Se atoms. The final pseudo-stoichiometry is  $\Psi$ -AsSe, adopting a structure in which butterfly-like  $[\text{Ge}_4]^{6-}$  anions ( $\Psi$ -AsSe) and vlasovite-like chains (also  $\Psi$ -AsSe) coexist (see Fig. 11b).

An example of an open-branched chain silicate is the mineral aenigmatite  $\text{Na}_2\text{Fe}_5\text{Ti}\{\text{oB}, 4, 1_{\infty}^1\}[\text{Si}_6\text{O}_{18}]\text{O}_2$  [66] (see Fig. 12a). In this case, the Na, Fe and Ti atoms donate 16 electrons per formula unit. Of them, 4 are directly transferred to two O atoms not bonded to silicon and the remaining 12 electrons go to the Si skeleton, converting two Si atoms into  $\Psi$ -P, two Si atoms into  $\Psi$ -S and two Si atoms into  $\Psi$ -Cl atoms. The final pseudo-formula would be  $\Psi$ - $\text{P}_2\text{S}_2\text{Cl}_2$  ( $\Psi$ -PSCl). Although there is no known Zintl phase with this type of structure, there are several compounds ( $\text{NaAsS}_2$ ,  $\text{NaAsSe}_2$ , ...) [67, 68] which have the same pseudo-stoichiometry, and they only differ slightly from aenigmatite in their atom arrangement. As can be seen in Fig. 12b, in the Zintl phases, every second atom of the stem of the chain carries a branch atom, whereas in the silicate two adjacent tetrahedra, each carrying a branch, alternate with the two tetrahedra without a branch. The chain periodicities, therefore, are  $P^C = 2$  and 4 for the Zintl phases and the silicate, respectively.

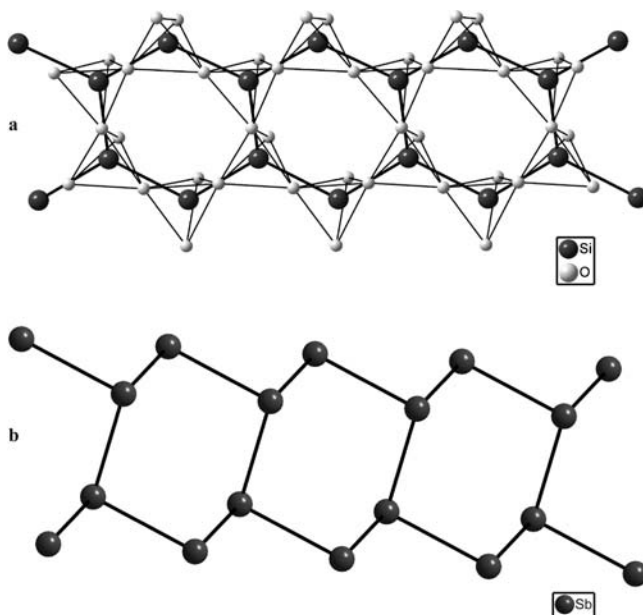


**Fig. 12** **a** The open-branched silicate chain in aenigmatite  $\text{Na}_2\text{Fe}_5\text{Ti}\{\text{oB}, 4, 1_{\infty}^1\}[\text{Si}_6\text{O}_{18}]\text{O}_2$ . The Si atoms behave as  $\Psi$ -P,  $\Psi$ -S and  $\Psi$ -Cl leading to the pseudo-stoichiometry  $\Psi$ -PSCl. **b** The strongly related chain formed by the Zintl polyanion  $\text{AsS}_2^-$  (also  $\Psi$ -PSCl) in  $\text{NaAsS}_2$

### 5.4.2

#### Double-Chain Silicates

Because amphiboles form one of the most abundant mineral groups, tremolite  $\text{Ca}_2\text{Mg}_5\{uB, 2, 2\frac{1}{\infty}\}[\text{Si}_8\text{O}_{22}](\text{OH})_2$  [12] is used to demonstrate the application of the Zintl-Klemm concept to unbranched *zweier* double chain silicates. The silicate anion of the amphibole is represented in Fig. 13a. In it, one half of its T atoms are three-connected and the other half two-connected. In this case, the Ca and Mg atoms together provide  $14 e^-$  per formula unit. Two of them are transferred directly to the hydroxyl groups and the remaining  $12 e^-$  should be transferred to the eight Si atoms, converting one half of them into  $\Psi$ -P (three-connected) and the other half into  $\Psi$ -S (two-connected). The result is an anion with a pseudo-stoichiometry  $\Psi$ -PS whose formula and structure are coincident with that observed in the Zintl polyanion  $[\text{Sb}_2]^-$  in the Zintl phase  $\text{KSb}_2$  [69]. This polyanion is represented in Fig. 13b. It is worth mentioning that this silicate anion can also be derived from the structure of As [70] in which the puckered layers are broken into fragments as a consequence of transforming one half of the atoms into  $\Psi$ -S. In fact, the double chain structure of the silicate resembles fragments of the chair-conformed layers of As.



**Fig. 13** (a) The double chain formed by the  $[\text{SiO}_4]$  tetrahedra in the amphibole tremolite,  $\text{Ca}_2\text{Mg}_5\{uB, 2, 2\frac{1}{\infty}\}[\text{Si}_8\text{O}_{22}](\text{OH})_2$ . The T atom skeleton is similar to that of the Sb atoms in the Zintl phase  $\text{KSb}_2$ , represented in (b)

## 5.5

### Layer Silicates

#### 5.5.1

##### Single-Layer Silicates

To this family of compounds belong the silicates which contain infinite two-dimensional layers of corner-sharing  $[\text{SiO}_4]$  tetrahedra. The layers contain  $n$ -membered rings, where  $n$  varies from 3, 4, 5, 6, 8 to 10 and more. In a few compounds, rings of different size coexist in the structure. Known ternary and quaternary compounds of this family are listed in Table 6 and divided into groups according to the branchedness and periodicity of the fundamental chains forming the layers.

#### 5.5.1.1

##### Silicon as Pseudo-P

We begin with compounds of stoichiometry  $\text{A}_2[\text{Si}_2\text{O}_5]$ . If we assume that two electrons per formula unit are transferred to the two Si atoms, these will be converted into pseudo-elements of the Group 15 of the PSE. In this way, a threefold connectivity is to be expected by applying the 8-N rule.

Thus, in  $\text{Li}_2[\text{Si}_2\text{O}_5]$  (*Pbcn*, *Ccc2*) [71, 72] and in  $\text{Na}_2[\text{Si}_2\text{O}_5]$  ( $\alpha$ : *Pbcn*,  $\beta$ :  $P2_1/a$ ) [73, 74], the Si atoms adopt structures formed by layers of chair conformed six-membered rings, similar to those existing in elemental As [70], GeS [75] or the As skeleton in claudetite, the monoclinic phase of  $\text{As}_2\text{O}_3$  [34]. If we consider the existence of these Si–Si bonds, three O atoms would be inserted close to the midpoints of the three Si–Si bonds. The fourth O atom would be situated close to the lone pair of the  $\Psi$ -P atoms. In this way, the tetrahedral coordination of silicon by the O atoms is obtained. This layer is represented in Fig. 14a to be compared with the layer of the As structure represented in Fig. 14b. Topologically identical layers with only three-connected tetrahedra which, however, contain either planar or boat conformed six-membered rings are present in some phyllosilicates, such as kaolinite, talc, pyrophyllite, sepiolite, etc ..., and in three other polymorphs of  $\text{Na}_2[\text{Si}_2\text{O}_5]$  ( $\delta$ :  $P2_1/n$ ,  $\varepsilon$ : *Pbc2*<sub>1</sub>,  $\zeta$ :  $P2_1/c$ ) [76–78] (see Table 6).

#### 5.5.1.2

##### The Pseudo- $\text{P}_2\text{S}_3$ Structure

Another structure to be discussed is that of  $\text{La}_3\text{Ga}^{[6]}[\text{Ga}_3^{[4][1;2]}\text{Ga}^{[4][1;3]}\text{Si}^{[4][1;3]}\text{O}_{14}]$  [79]. The structure contains one hexa-coordinated Ga atom per formula unit, whereas the other four Ga atoms and the Si atom are tetra-coordinated (the so called T atoms). The electron transfer which justifies

**Table 6**

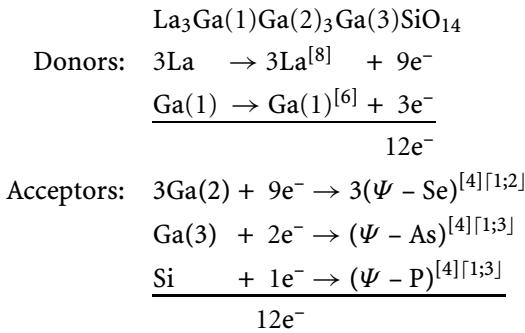
		Layer silicates				
		Single-layer silicates				
		Unbranched single-layer silicates				
		{ <i>uB</i> , 1 <sub>∞</sub> <sup>2</sup> }, Pseudo-Si <sub>k</sub> P <sub>l</sub> S <sub>m</sub> Cl <sub>n</sub>				
Mineral name	Formula	<i>P</i> <sup>C</sup>	<i>k</i>	<i>l</i>	<i>m</i>	<i>n</i> Ref.
Kanemite	HA[Si <sub>2</sub> O <sub>5</sub> ] with A = H, K, Rb, Cs	2	0	2	0	0 [320a–c]
	HNa[Si <sub>2</sub> O <sub>5</sub> ](H <sub>2</sub> O) <sub>3</sub>	2	0	2	0	0 [321]
	Li A[Si <sub>2</sub> O <sub>5</sub> ]* with A = Li, K	2	0	2	0	0 [322a–c]
Petalite	LiAl[Si <sub>4</sub> O <sub>10</sub> ]*	2	0	2	0	0 [323]
	K <sub>2</sub> [Si <sub>4</sub> O <sub>9</sub> ] (LP)	2	2	2	0	0 [324]
Micas, e.g. annite, muscovite	KFe(II) <sub>3</sub> [AlSi <sub>3</sub> O <sub>10</sub> ](OH) <sub>2</sub>	2	0	4	0	0 [325]
	KAl <sub>3</sub> [AlSi <sub>3</sub> O <sub>10</sub> ](OH) <sub>2</sub>	2	0	4	0	0 [326]
Talc	Mg <sub>3</sub> [Si <sub>2</sub> O <sub>5</sub> ] <sub>2</sub> (OH) <sub>2</sub>	2	0	2	0	0 [327]
Sanbornite	Ba[Si <sub>2</sub> O <sub>5</sub> ]	2	0	2	0	0 [328]
Kaolinite, nacrite, dickite	Al <sub>2</sub> [Si <sub>2</sub> O <sub>5</sub> ](OH) <sub>4</sub>	2	0	2	0	0 [329a–c]
Apophyllite	Na <sub>3</sub> K <sub>3</sub> [Si <sub>6</sub> O <sub>15</sub> ]	3	0	6	0	0 [330]
	ACa <sub>4</sub> [Si <sub>8</sub> O <sub>20</sub> ](X(H <sub>2</sub> O) <sub>8</sub> ) with A = Na, K; X = F, OH	4	0	8	0	0 [331]
Pentvilsite	Na <sub>4</sub> Zn <sub>2</sub> [Si <sub>6</sub> O <sub>16</sub> ]*	3	0	4	2	0 [332]
	Na <sub>4</sub> Ti <sub>2</sub> [Si <sub>8</sub> O <sub>22</sub> ](H <sub>2</sub> O) <sub>4</sub>	4	0	4	4	0 [333]
	K <sub>2</sub> Ba <sub>7</sub> [Si <sub>8</sub> O <sub>20</sub> ] <sub>2</sub>	4	0	8	0	0 [334]
Davanite, dalyite	K <sub>2</sub> A[Si <sub>6</sub> O <sub>15</sub> ] with A = <u>Ti</u> , <u>Zr</u>	3	0	6	0	0 [335]
Cuprorivaite, wesselsite, effenbergerite	A <sub>2</sub> Cu <sub>2</sub> [Si <sub>8</sub> O <sub>20</sub> ] with A = <u>Ca</u> , <u>Sr</u> , <u>Ba</u> ,	4	0	8	0	0 [336a–c]
Ekanite	Ca <sub>2</sub> Th[Si <sub>8</sub> O <sub>20</sub> ]	4	0	8	0	0 [337]
	LiBa <sub>9</sub> [Si <sub>10</sub> O <sub>25</sub> ]Cl <sub>7</sub> (CO <sub>3</sub> )	5	0	10	0	0 [338]
	K <sub>12</sub> [Si <sub>12</sub> O <sub>30</sub> ]	6	0	12	0	0 [322b]
Manganpyrosmalite	(Mn, Fe) <sub>16</sub> [Si <sub>12</sub> O <sub>30</sub> ](OH) <sub>17</sub> Cl <sub>3</sub>	6	0	12	0	0 [339]
Open-branched single-layer silicates		{ <i>oB</i> , 1 <sub>∞</sub> <sup>2</sup> } Pseudo-Si <sub>k</sub> P <sub>l</sub> S <sub>m</sub> Cl <sub>n</sub>				
Prehnite	Ca <sub>2</sub> (Al, Fe)[AlSi <sub>3</sub> O <sub>10</sub> ](OH) <sub>2</sub>	2	2	0	2	0 [340]
Kvanefeldite	H <sub>2</sub> Na <sub>4</sub> (Ca, Mn)[Si <sub>6</sub> O <sub>16</sub> ]	4	0	4	2	0 [341]
Zeophyllite	Ca <sub>13</sub> [Si <sub>5</sub> O <sub>14</sub> ] <sub>2</sub> F <sub>10</sub> (H <sub>2</sub> O) <sub>6</sub>	4	0	2	3	0 [342]
	La <sub>3</sub> Ga <sup>[6]</sup> [Ga <sub>4</sub> SiO <sub>14</sub> ]	4	0	2	3	0 [343]
Loop-branched single-layer silicates		{ <i>IB</i> , 1 <sub>∞</sub> <sup>2</sup> } Pseudo-Si <sub>k</sub> P <sub>l</sub> S <sub>m</sub> Cl <sub>n</sub>				
Zussmanite	Na <sub>6</sub> [Si <sub>8</sub> O <sub>19</sub> ]	2	2	6	0	0 [344]
	NaA[Si <sub>6</sub> O <sub>14</sub> ] with A = Pr, Nd	4	2	4	0	0 [345]
	K <sub>4</sub> Sb <sub>2</sub> [Si <sub>8</sub> O <sub>20</sub> ](OH) <sub>2</sub>	3	0	8	0	0 [346]
	K <sub>2</sub> Ge[Si <sub>6</sub> O <sub>15</sub> ]	4	0	6	0	0 [347]
	KFe <sub>13</sub> [AlSi <sub>17</sub> O <sub>42</sub> ](OH) <sub>4</sub>	5	6	12	0	0 [348]
	K <sub>8</sub> Yb <sub>3</sub> [Si <sub>6</sub> O <sub>16</sub> ] <sub>2</sub> (OH)	5	0	4	2	0 [349]
	K <sub>2</sub> Eu(II) <sub>4</sub> [Si <sub>8</sub> O <sub>20</sub> ]F <sub>2</sub>	6	0	8	0	0 [350]

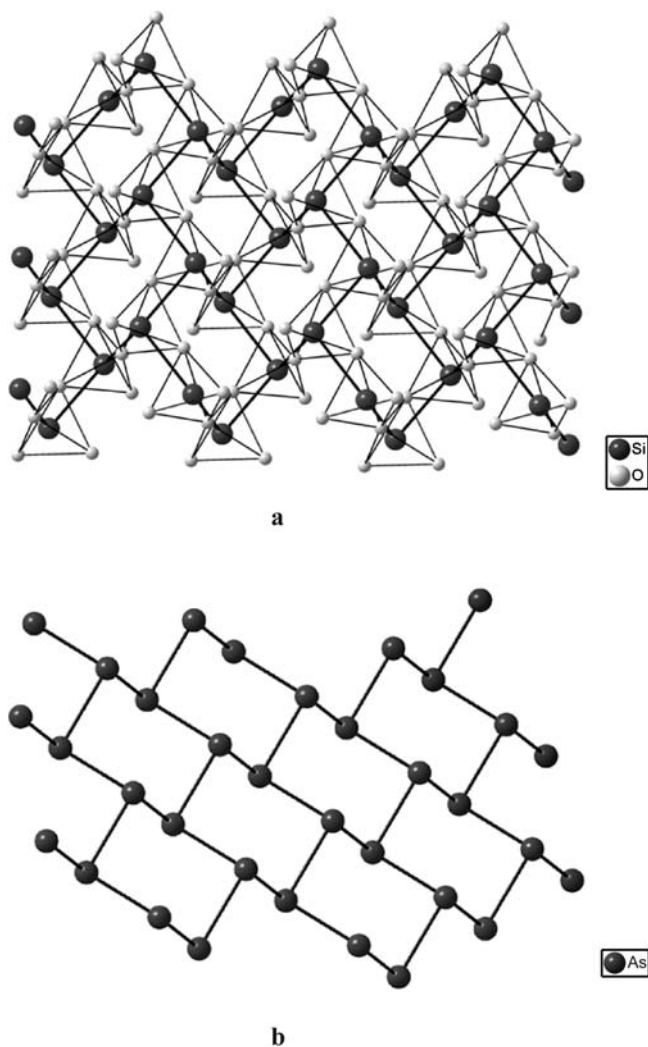
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**Table 6** (continued)

Mineral name	Formula	$P^C$	$k$	$l$	$m$	$n$	Ref.
Double-layer silicates							
Unbranched double-layer silicates							
{ <i>uB</i> , 2 <sub>∞</sub> <sup>2</sup> } Pseudo-Si <sub>k</sub> P <sub>l</sub> S <sub>m</sub> Cl <sub>n</sub>							
Dmisteinbergite, cymrite	A[Al <sub>2</sub> Si <sub>2</sub> O <sub>8</sub> ](H <sub>2</sub> O) <sub>1–x</sub> with A = <u>Ca</u> , Sr, <u>Ba</u>	2	4	0	0	0	[351a–c]
Open-branched double-layer silicates							
{ <i>oB</i> , 2 <sub>∞</sub> <sup>2</sup> } Pseudo-Si <sub>k</sub> P <sub>l</sub> S <sub>m</sub> Cl <sub>n</sub>							
	[C <sub>4</sub> H <sub>12</sub> N <sub>2</sub> <sup>2+</sup> ][Si <sub>6</sub> O <sub>13</sub> ]	2	4	2	0	0	[352]
Loop-branched double-layer silicates							
{ <i>lB</i> , 2 <sub>∞</sub> <sup>2</sup> } Pseudo-Si <sub>k</sub> P <sub>l</sub> S <sub>m</sub> Cl <sub>n</sub>							
Rhodesite	HKCa <sub>2</sub> [Si <sub>8</sub> O <sub>19</sub> ](H <sub>2</sub> O) <sub>5</sub>	3	2	6	0	0	[353]
Macdonaldite	H <sub>2</sub> Ca <sub>4</sub> Ba[Si <sub>8</sub> O <sub>19</sub> ] <sub>2</sub> (H <sub>2</sub> O) <sub>10</sub>	3	2	6	0	0	[354]
Delhayelite	Na <sub>3</sub> K <sub>7</sub> Ca <sub>5</sub> [AlSi <sub>7</sub> O <sub>19</sub> ] <sub>2</sub> Cl <sub>2</sub> F <sub>4</sub>	3	2	6	0	0	[355]
	Cs <sub>3</sub> Sc[Si <sub>8</sub> O <sub>19</sub> ]	3	2	6	0	0	[356]
Carletonite	KNa <sub>4</sub> Ca <sub>4</sub> [Si <sub>8</sub> O <sub>18</sub> ](F,OH)(CO <sub>3</sub> ) <sub>4</sub> (H <sub>2</sub> O)	6	4	4	0	0	[357]

the observed structure of the gallosilicate layer is summarised in the following scheme:





**Fig. 14** (a) A layer of  $[\text{Si}_2\text{O}_5]^{2-}$  anions in  $\alpha\text{-Na}_2[\text{Si}_2\text{O}_5]$  (*Pbcn*) in which the Si atoms adopt the layer structure of As, drawn in (b)

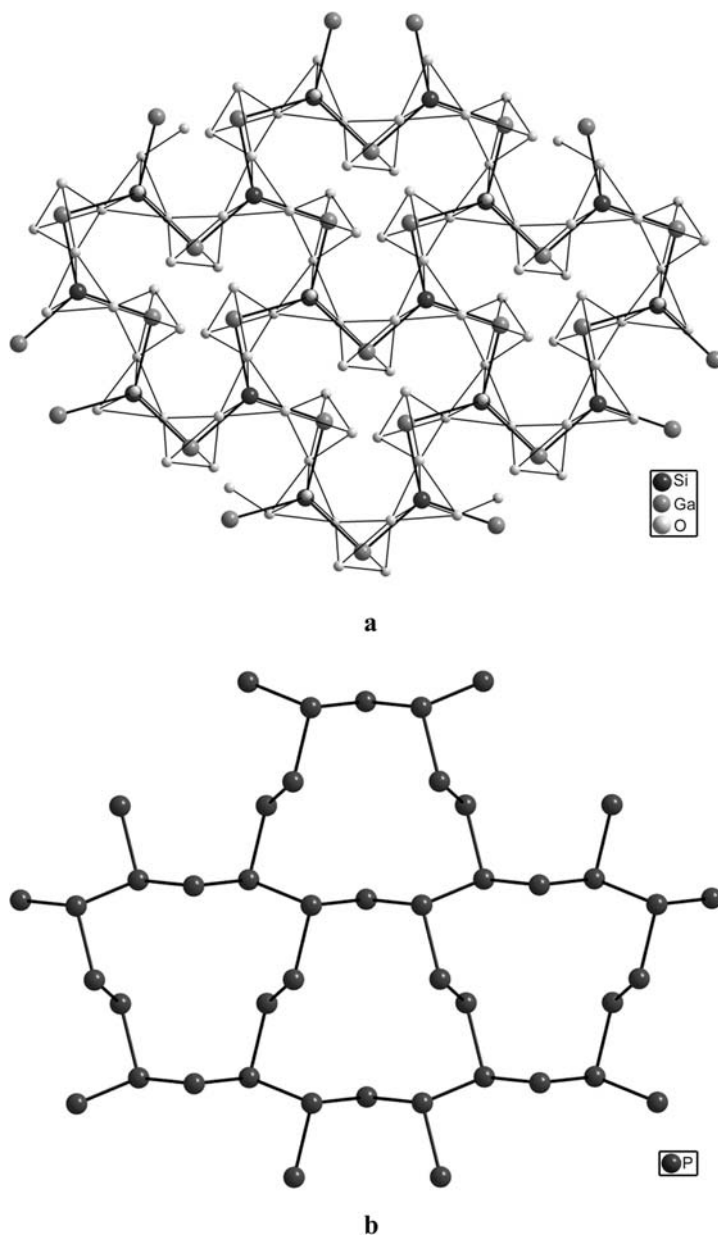
ated close to bonding and lone electron pairs giving rise to the tetrahedral coordination.

### 5.5.1.3

#### Dual Role of T Atoms other than Si and Al

There is an ambiguity whether tetrahedrally coordinated cations T other than Si and Al are considered to be part of the silicate anions or not.





**Fig. 15** (a) The structure of the  $[\text{Ga}_4\text{SiO}_{14}]^{12-}$  layer in  $\text{La}_3\text{Ga}^{[6]}[\text{Ga}_3^{[4]1;3}]\text{Ga}^{[4]1;2}]\text{Si}^{[4]1;3}]\text{O}_{14}$ . The Ga – Si subarray forms a net of  $\Psi\text{-P}_2\text{S}_3$  (or more accurately  $\Psi\text{-PAsSe}_3$ ) pseudo stoichiometry in which the  $\Psi\text{-P}$  atoms are three-connected and the  $\Psi\text{-S}$  atoms are two-connected. O atoms are located near to the bonding and lone pair electron positions. This planar layer is strongly related to the corrugated layer formed by the P atoms in  $\text{CeP}_5$  which is represented in (b)

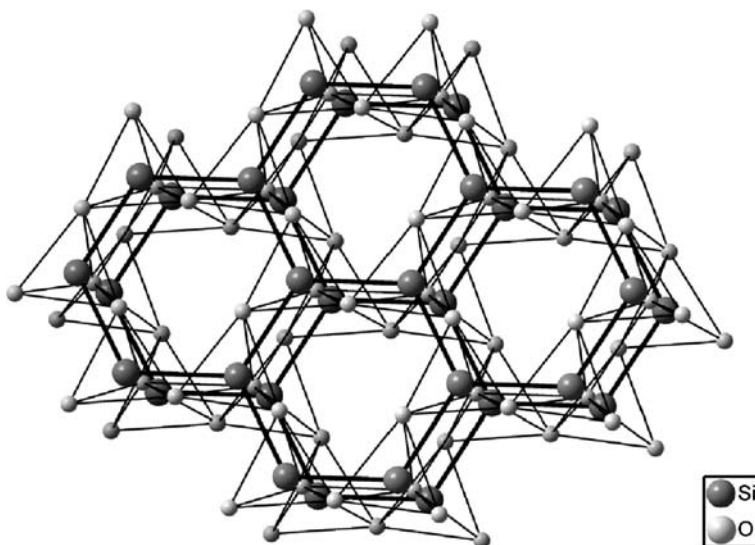
For example,  $\text{Na}_2\text{ZnSi}_3\text{O}_8$  [81] can be considered as a single-layer silicate  $\text{Na}_4\text{Zn}_2\{\text{I}_{\infty}^2\}[\text{Si}_6\text{O}_{16}]$  if only the Si skeleton is taken into account. However, the compound can also be seen as a tectosilicate  $\text{Na}_4\{\text{I}_{\infty}^3\}[\text{Zn}_2\text{Si}_6\text{O}_{16}]$  if the tetrahedrally coordinated Zn atoms are included in the T atom framework. In this case, the four Na atoms per formula unit would convert the two Zn atoms into  $\Psi$ -Si. This dual role of T atoms other than Si and Al, can occur in other compounds as well. For example,  $\text{K}_2\text{ZnSi}_2\text{O}_6$  can either be classified as a chain silicate  $\text{K}_4\text{Zn}_2\{\text{I}_{\infty}^1\}[\text{Si}_4\text{O}_{12}]$  with unbranched *vierer* single chains or as a tectosilicate  $\text{K}_2\{\text{I}_{\infty}^3\}[\text{ZnSi}_2\text{O}_6]$  [82]. In Tables 6–7, corresponding examples have been indicated with \*.

### 5.5.2

#### Double-Layer Silicates

A small number of compounds have been found to contain silicate anions which can be regarded as a product of the condensation of two single layers. Compounds presenting this kind of framework are also collected in Table 6.

An example of these compounds is provided by the mineral dmisteinbergite,  $\text{Ca}[\text{Al}_2\text{Si}_2\text{O}_8]$  [83] which has previously been called hexacelsian. Its T-atom subarray is a double layer. Each of the two single layers contains only six-membered planar rings, corresponding to the single layers of carbon atoms in graphite. Each T atom of one single layer is “linked” to a T atom



**Fig. 16** The double layer formed by the aluminosilicate anion in dmisteinbergite,  $\text{Ca}[\text{Al}_2\text{Si}_2\text{O}_8]$ . The Ca atoms convert the Al atoms into  $\Psi$ -Si giving rise to a net in which all the Al and Si atoms are four-connected

of the other, as seen in Fig. 16. This skeleton can be explained as a consequence of the electron transfer from calcium to aluminium which is converted into  $\Psi$ -Si, thus forming a four-connected net. It is worth mentioning that this skeleton is almost identical to that of the Zintl phases  $\text{CaAl}_2\text{Si}_2$  [84] and  $\text{CaAl}_2\text{Ge}_2$  [85] and that, as reported previously [86], the structure of dmisteinbergite can be derived from that of the Zintl phase by inserting one O atom between each pair Al – Si. It is also interesting to point out that these minerals are high temperature phases. At room temperature the structure of feldspar is obtained. This can be interpreted in the light of the equivalence between oxidation and pressure [63]. Thus, oxidation could stabilise a high pressure polymorph of the Zintl phase which would correspond to the cation array of feldspar. When heated, the pressure can be released and the ambient pressure polymorph of the Zintl phase is recovered in dmisteinbergite.

## 5.6

### Tectosilicates

#### 5.6.1

##### Subdivision of Tetrahedron Frameworks According to Connectivity

All silicates in which  $[\text{TO}_4]$  tetrahedra form 3D tetrahedron frameworks by sharing oxygen atoms are called tectosilicates. The vast majority of tectosilicates contain only four-connected tetrahedra so that each framework oxygen atom is linked to two T atoms and is, therefore, two-connected. As a consequence, the ratio between T atoms and framework O (or more generally X) atoms in the unit cell uc is  $z = \sum_{\text{uc}} n(\text{O}) / \sum_{\text{uc}} n(\text{T}) = 2$ . For such tectosilicates the term *fully linked* tectosilicates has been suggested [87, p 50].

There is a relatively small number of tectosilicates which contain  $[\text{TO}_4]$  tetrahedra that are linked to less than four others, i.e. which contain, exclusively or in addition to 3-connected  $\text{Q}^3$  units, also  $\text{Q}^4$  units and, very rarely, also  $\text{Q}^2$  and  $\text{Q}^1$  tetrahedra. These silicates necessarily contain non-bridging framework O atoms and their atomic ratio  $z$  is higher than 2. For them the term *underlinked* tectosilicates has been proposed [87, p 50f]. They are often, but less accurately, called interrupted framework silicates.

#### 5.6.2

##### Fully Linked Tectosilicates

In fully linked tectosilicates, the cation ratio  $n(\text{A}) : n(\text{T})$  is relatively low. The valence electrons of their A atoms serve to compensate the negative valence of the tetrahedron framework that results from partial replacement of tetrahedrally coordinated  $\text{Si}^{4+}$  atoms by T atoms of lower valence, such as  $\text{Al}^{3+}$  and  $\text{Zn}^{2+}$ . This is the case in all examples given in the main part of Table 7.

**Table 7**

Tectosilicates		
Tectosilicates with fully-linked tetrahedron frameworks		
$\{\infty^3\}$ Pseudo-Si		
Mineral name	Formula	Ref.
Stuffed quartz-type silicates		
Virgilite	A[AlSi <sub>2</sub> O <sub>6</sub> ] with A = H, <u>Li</u>	[358a–b]
( $\beta$ -Eucryptite)	Li[AlSiO <sub>4</sub> ]	[359]
	Mg[Al <sub>2</sub> Si <sub>3</sub> O <sub>10</sub> ]	[360]
Stuffed cristobalite-type and cristobalite related silicates		
Liberite	Li <sub>2</sub> [BeSiO <sub>4</sub> ]*	[361]
(Carnegieite)	Na[AlSiO <sub>4</sub> ]	[362]
	Li[BSiO <sub>4</sub> ]*	[363]
Chkalovite	Na <sub>2</sub> [TSiO <sub>4</sub> ]* with T = <u>Be</u> , Mg	[364a–c]
	Na <sub>2</sub> [ZnSi <sub>2</sub> O <sub>6</sub> ]*	[365]
	Ba[BeSiO <sub>4</sub> ]*	[366]
Stuffed tridymite-type and tridymite related silicates		
Nepheline, trinepheline, kalsilite, megakalsilite, kaliophilite	A[AlSiO <sub>4</sub> ] with A = <u>Na</u> , <u>K</u>	[367a–e]
Yoshiokaite	(Ca),[(AlSi) <sub>2</sub> O <sub>4</sub> ]	[368]
Stuffed keatite-type silicates		
	A[AlSi <sub>2</sub> O <sub>6</sub> ] with A = Li, Na, K	[369]
Stuffed SrAl <sub>2</sub> -type silicates		
	Li <sub>2</sub> [TSiO <sub>4</sub> ]* with T = Co, Zn	[370a–b]
	K <sub>2</sub> [ZnSi <sub>3</sub> O <sub>8</sub> ]*	[371]
	Rb[AlSiO <sub>4</sub> ]	[372]
Stuffed zeosils		
Zeolites, e.g. natrolite, chabazite, faujasite, mordenite	A <sub>m</sub> [(T, Si) <sub>n</sub> O <sub>2n</sub> ] with T = Be, Mg, Zn, B, Al, [373a–b] Ga, Fe, Co, Cr, Ge, P	
Feldspar-type silicates		
Feldspars, e.g. albite, orthoclase, microcline, anorthite, celsian, danburite, Reedmergnerite	A[(T, Si) <sub>4</sub> O <sub>8</sub> ]* with T = B, Al, Ga, Fe, Ge, P	[374a–h]
Other silicates with fully-linked [TO <sub>2</sub> ] frameworks		
	Li <sub>4</sub> [B <sub>4</sub> Si <sub>8</sub> O <sub>24</sub> ]*	[375]
	$\beta$ -Na <sub>2</sub> [BeSiO <sub>4</sub> ]*	[376]
	K <sub>2</sub> [ZnSi <sub>2</sub> O <sub>6</sub> ]*	[377]
Litidionite	(Na, K) <sub>2</sub> [CuSi <sub>4</sub> O <sub>10</sub> ]*	[378]
	Cs[AlSi <sub>5</sub> O <sub>12</sub> ]	[379]
Cordierite	A <sub>2</sub> [Al <sub>4</sub> Si <sub>5</sub> O <sub>18</sub> ] with A = <u>Mg</u> , Co, Mn, Fe	[380a–e]
Cuprorivaite, wesselite, effenbergerite	A <sub>2</sub> [Cu <sub>2</sub> Si <sub>8</sub> O <sub>20</sub> ]* with A = <u>Ca</u> , <u>Sr</u> , <u>Ba</u>	[381]
Beryl	Mg <sub>2</sub> [Be <sub>3</sub> Si <sub>6</sub> O <sub>18</sub> ](H <sub>2</sub> O) <sub>x</sub> *	[382]

**Table 7** (continued)

Mineral name	Formula	<i>k</i>	<i>l</i>	<i>m</i>	<i>n</i>	Ref.
Tectosilicates with underlinked tetrahedron frameworks						
	$\{\infty\}^3$ Pseudo-Si <sub>k</sub> P <sub>l</sub> S <sub>m</sub> Cl <sub>n</sub>					
Wenkite	H <sub>2</sub> Ca <sub>3</sub> Ba <sub>4</sub> [(Al <sub>8</sub> Si <sub>12</sub> )O <sub>41</sub> ](SO <sub>4</sub> ) <sub>3</sub> (H <sub>2</sub> O)	18	2	0	0	[383]
Chiavennite	H <sub>2</sub> CaMn[Be <sub>2</sub> <sup>[1,3]</sup> Si <sub>5</sub> <sup>[1,4]</sup> O <sub>15</sub> ](H <sub>2</sub> O) <sub>2</sub>	5	2	0	0	[384]
	Na <sub>4</sub> [Si <sub>6</sub> O <sub>14</sub> ]	2	4	0	0	[385]
	K <sub>2</sub> Ce[Si <sub>6</sub> O <sub>15</sub> ]	0	6	0	0	[386]
	Rb <sub>6</sub> [Si <sub>10</sub> O <sub>23</sub> ]	4	6	0	0	[387]
	Ce <sub>4</sub> [Si <sub>4</sub> O <sub>4</sub> N <sub>6</sub> ]O	0	4	0	0	[388]

### 5.6.2.1

#### Relationship between the Frameworks of Fully Linked Tectosilicates and Silica

The most simple oxides matching the relation  $z = \sum_{uc} n(O) / \sum_{uc} n(T) = 2$  are the binary silica polymorphs with the exception of those HP polymorphs in which silicon has coordination numbers higher than four, i.e. stishovite, distorted stishovite and CaF<sub>2</sub>-type silica. In all known SiO<sub>2</sub> phases with tetrahedrally coordinated Si atoms, each O atom is shared between two [SiO<sub>4</sub>] tetrahedra. This leads necessarily to the formation of a 3D framework. As mentioned in the introduction and as reported previously [8], these 3D tetrahedron frameworks and their corresponding 3D Si-atom subarrays are four-connected and maintain the structure of elemental phases of either silicon or other elements of Group 14 of the PSE.

Some quaternary tectosilicates are considered as stuffed derivatives of quartz, cristobalite, tridymite, keatite and chabazite, and their Si-substructures (with the exception of chabazite) reproduce the structure of phases of either elements of Group 14 of the PSE, Si and Ge, or compounds which are intimately related to them. Thus, the diamond-like structure of the Si subarray is found in cristobalite, the wurtzite-like structure of Si appears in tridymite, keatite reproduces the structure of  $\gamma$ -Ge. In quartz, the Si atoms adopt the structure of the related compound CrSi<sub>2</sub> [23] and also the cinnabar-like structure of the high pressure II–VI compounds such as ZnTe [24].

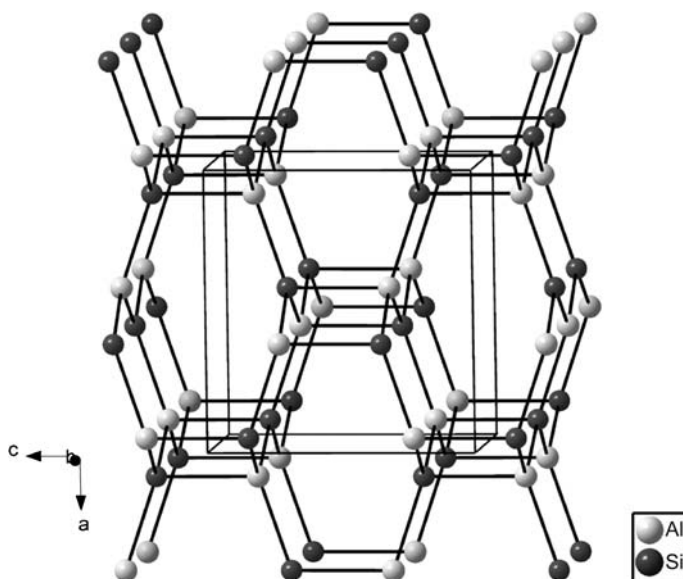
Other groups of silicates adopt very complicated frameworks which maintain the fourfold connectivity. For them, no structural relationship has been found with similar Zintl phases. However, all of them fulfil the Zintl–Klemm concept when applied to the element which accompanies the Si atom in the tetrahedral framework.

The remaining compounds present interesting structural similarities and some of them will be discussed below.

### 5.6.2.2

#### The $\text{SrAl}_2$ -type Skeleton

These compounds, such as  $\text{Rb}[\text{AlSiO}_4]$  [88] (see Table 7), form 3D tetrahedron frameworks consisting of four- and eight-membered rings which give rise to a fourfold connectivity. The structure is represented in Fig. 17. Although no phase of the Group 14 elements is known to have this structure, it is identical to that adopted by the Al ( $\Psi$ -Si) atoms in the Zintl phase  $\text{SrAl}_2$  [89]. The O atoms are located near to the centres of all the Al – Si bonds producing the tetrahedral coordination of the Al(Si) atoms. Once more, the cation subarray, in an oxide, behaves as if it were a Zintl polyanion.

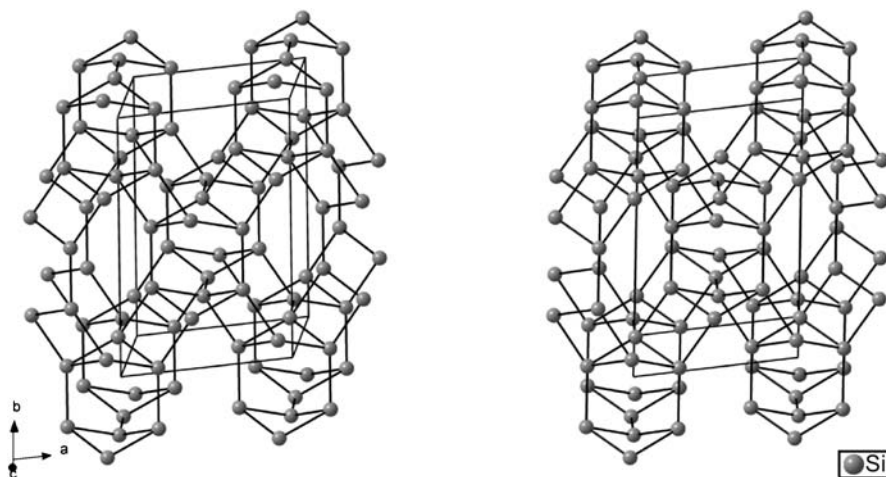


**Fig. 17** The structure of the T-atom subframework of  $\text{Rb}[\text{AlSiO}_4]$ . The AlSi subarray is similar to that existing in the Zintl phase  $\text{SrAl}_2$  where the Al atoms have been converted into  $\Psi$ -Si, and all atoms are four-connected

### 5.6.2.3

#### The Feldspar Structure

Compounds belonging to this group are also listed in Table 7. All of them are borosilicates and aluminosilicates in which the B, Al and Si atoms form a 3D framework of four-connected tetrahedra. Consequently, the T atom skeleton is also four-connected (Fig. 18). It is remarkable that the structures of feldspars and that of coesite ( $\text{SiO}_2$  polymorph) are similar. This seems to be reasonable because, in compounds such as slawsonite  $\text{Sr}[\text{Al}_2\text{Si}_2\text{O}_8]$  [90], and reedmergnerite  $\text{Na}[\text{BSi}_3\text{O}_8]$  [91], the electropositive cations convert the Al



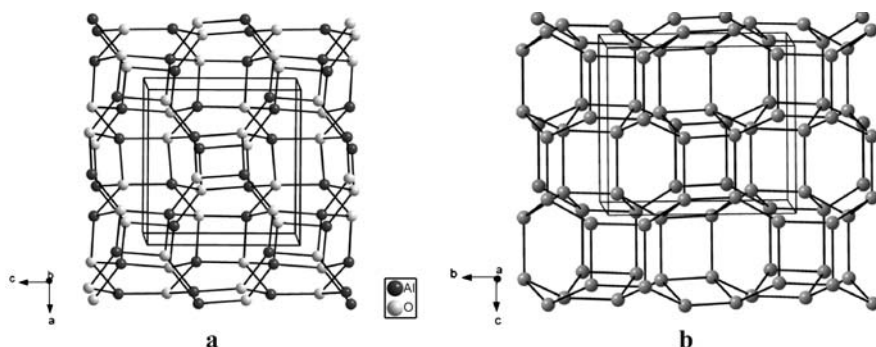
**Fig. 18** Stereopair showing the 3D T-atom subarray of the feldspar  $\text{Rb}[\text{AlSi}_3\text{O}_8]$ . As seen all the Al and Si atoms are four-connected

and B atoms into  $\Psi$ -Si/C atoms giving rise to a framework of stoichiometry  $\text{TO}_2$ .

#### 5.6.2.4

##### Paracelsian and Variscite

Variscite [92] is the mineral name of one of the two phases of  $\text{AlPO}_4 \cdot 2\text{H}_2\text{O}$ , the other being metavariscite [93]. Its AlP subarray forms a 3D four-connected framework in which each Al atom is connected to four P atoms and vice versa. A projection of the structure is represented in Fig. 19a. This array shows strong similarities with the structure of paracelsian  $\text{Ba}[\text{Al}_2\text{Si}_2\text{O}_8]$  [94] which is also adopted by the isostructural compounds  $\text{Ca}[\text{B}_2\text{Si}_2\text{O}_8]$  (danburite) [95],  $\text{K}[\text{BSi}_3\text{O}_8]$  [96] and  $\text{Na}_2[\text{ZnSi}_3\text{O}_8]$  [97]. The AlSi subarray of the paracelsian is represented in Fig. 19b. It is formed by four-, six-, and eight-membered rings. Again, there are strong similarities between the T atom framework of these silicates and the arrays of III–V oxidic compounds such as  $\text{AlPO}_4 \cdot 2\text{H}_2\text{O}$ . In the light of the Zintl–Klemm concept this means that a  $\Psi$ -Si array is formed when the electropositive atoms donate their valence electrons to the more electronegative B, Zn and Al atoms. It should be remarked that this framework has never been observed, neither in any of the phases of silica nor in the HP phases of silicon, and that only fragments of this net exist in the form of small organic molecules [8]. Here the question arises again whether this skeleton is only stable for oxidic III–V compounds such as variscite or, on the contrary, can also be stable in phases of the elements of Group 14 of the PSE.



**Fig. 19** **a** The AlP network in variscite  $\text{AlPO}_4 \cdot 2\text{H}_2\text{O}$ . This III-V net adopts a fourfold connectivity characteristic of the IV-IV compounds. **b** The AlSi network in paracelsian  $\text{Ba}[\text{Al}_2\text{Si}_2\text{O}_8]$ . The Ba atoms convert the Al atoms into  $\Psi$ -Si which together with the Si atoms form a four-connected net similar to that of variscite (**a**)

It is worth mentioning that the structure of paracelsian has been related to that of metavariscite [98]. However, an inspection of three projections of the paracelsian structure reveals that two of them are strongly related with the other two projections of variscite and that, in fact, paracelsian must be considered as an intermediate structure between the two phases of  $\text{AlPO}_4 \cdot 2\text{H}_2\text{O}$ .

### 5.6.3

#### Underlinked Tectosilicates

If the cation ratio  $n(\text{A}) : n(\text{T})$  increases, an excess of valence electrons becomes available that can be transferred to T atoms to produce pseudo-atoms in agreement with the Zintl–Klemm concept. Examples of such underlinked tectosilicates are listed in the last part of Table 7. For instance, in the zeolite chivennite,  $\text{H}_2\text{CaMn}(\text{II})[\text{Be}_2\text{Si}_5\text{O}_{15}](\text{H}_2\text{O})_2$  [99], the non-tetrahedral cations can transfer six valence electrons per formula unit to the Be atoms, transforming them into  $\Psi$ -P atoms. As a result, the two  $[\text{BeO}_4]$  tetrahedra are 3-connected whereas the five  $[\text{SiO}_4]$  tetrahedra are 4-connected.

Another two examples of underlinked silicates are the compounds  $\text{Ce}_4[\text{Si}_4\text{O}_4\text{N}_6]\text{O}$  and  $\text{K}_2\text{Ce}[\text{Si}_6\text{O}_{15}]$  in which the Si atoms present a threefold connectivity.

In  $\text{Ce}_4[\text{Si}_4\text{O}_4\text{N}_6]\text{O}$  [100], the four trivalent Ce atoms per formula unit provide 12 valence electrons. Two of them are transferred directly to an O atom not bonded to silicon,  $6 e^-$  must be considered as extra electrons to be transferred to the six N atoms if they are compared with the O atoms. The remaining  $4 e^-$  serve to transform the four Si atoms into  $\Psi$ -P which, as said above, are three-connected.



The same can be said of  $\text{K}_2\text{Ce}[\text{Si}_6\text{O}_{15}]$  [101]; the six valence electrons per formula unit provided by K and tetravalent Ce atoms serve to convert the six Si atoms into  $\Psi$ -P, with the corresponding threefold connectivity.

It should be remembered that in the Zintl phase  $\text{SrSi}_2$ , the  $\Psi$ -P atoms also form a 3D array with three-connected atoms, although the skeleton is not similar to those of the compounds discussed here.

## 6

### Si Atoms in Octahedral Coordination

A general survey of hexa-coordinated silicon compounds has been reported by Finger and Hazen [102].

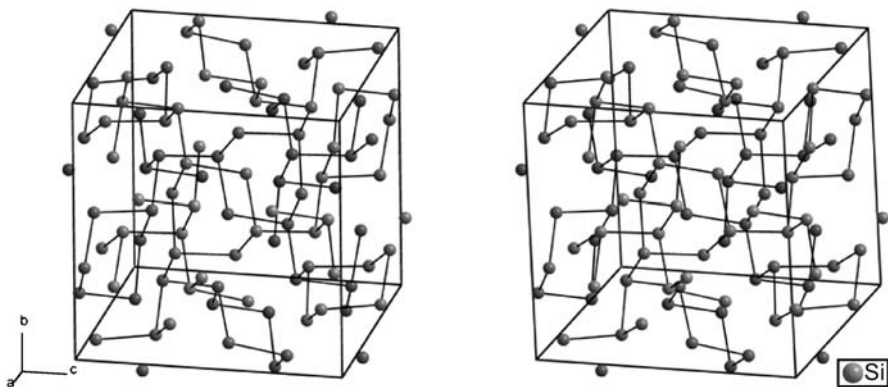
Previously we have discussed that in some silicates, as a result of the amphoteric behaviour of the Si atoms, part or all of the silicon atoms are hexa-coordinated whereas the others have the normal tetrahedral coordination. We must refer here again to the compounds  $\text{Na}_2\text{Si}^{[6]}\{\text{t}\}[\text{Si}_2^{[4]}\text{O}_7]$  [39],  $\text{K}_2\text{Si}^{[6]}\{\text{uB},1\text{r}\}[\text{Si}_3^{[4]}\text{O}_9]$  [52],  $\text{Na}_8\text{Si}^{[6]}\{\text{uB},1\text{r}\}[\text{Si}_6^{[4]}\text{O}_{18}]$  [53] and  $\text{Na}_6\text{Si}_3^{[6]}\{\text{uB},1\text{r}\}[\text{Si}_9^{[4]}\text{O}_{27}]$  [54] discussed previously. The first compound was discussed in Sect. 5.2.1. It should be remembered that this HP phase contains one hexa-coordinated Si atom and two tetra-coordinated Si atoms per formula unit which form a disilicate anion  $[\text{Si}_2\text{O}_7]^{6-}$ . The other three silicates were discussed in Sect. 5.3.1 devoted to ring silicates. The first one contains one hexa-coordinated Si atom, the other three four-coordinated Si atoms forming a three-membered ring  $[\text{Si}_3\text{O}_9]^{6-}$ . The next phase presents one hexa-coordinated Si atom per formula unit, whereas the remaining six Si atoms form a six-membered ring  $[\text{Si}_6\text{O}_{18}]^{12-}$ . In the last one, also a HP phase, there are three donor, hexa-coordinated Si atoms which coexist with a nine-membered planar ring.

Thus, a donor behaviour of Si leads to an octahedral coordination whereas the acceptor character produces the tetrahedral coordination. This trend is clearly seen in the various polymorphs of silicon oxophosphate  $\text{SiP}_2\text{O}_7$  [103–106] which contain all their silicon atoms in octahedral coordination, even though they are not high-pressure phases. It has been pointed out [107] that the tendency of silicon to form  $[\text{SiO}_6]$  octahedra instead of  $[\text{SiO}_4]$  tetrahedra is due to the stronger electronegativity of the central oxoanion atom (in this case phosphorus). Thus,  $\text{SiP}_2\text{O}_7$  is a clear example of how the donor character of silicon leads to octahedral coordination of silicon. On the other hand,  $\text{SiP}_2\text{O}_7$  can also be described by application of the Zintl–Klemm concept. Since P is more electronegative than Si, each of the two P atoms per formula unit subtracts two valence electrons from Si in order to become a  $\Psi$ -halogen atom. Therefore,  $\text{Si}^{[6]}\text{P}_2^{[4]}\text{O}_7$  can be compared with the disilicates such as thortveitite, the  $\text{Sc}_2^{[6]}\text{Si}_2^{[4]}\text{O}_7$  phase which is stable at ambient

P/T conditions [108]. In this silicate, Si is more electronegative than Sc and, therefore, subtracts the valence electrons from Sc to form  $\Psi$ -halogen atoms.

The compound  $\text{Ce}_{16}\text{Si}^{[6]}[\text{Si}_{14}^{[4]}\text{O}_6\text{N}_{32}]$  is of special interest. It is an oxonitridosilicate with silicon partly coordinated by nitrogen [109]. It has been considered by the authors as strongly related to the perovskite type  $\text{A}^{[12]}\text{G}^{[6]}\text{X}_3$ . Its unit cell can be considered as a cubic  $4 \times 4 \times 4$  superstructure of the ideal cubic perovskite in which, of the 64 octahedral positions per unit cell, four are occupied by  $\text{Si}^{[6]}$ , 56 by  $\text{Si}^{[4]}$  and four G positions are unoccupied. In contrast, the 64 cuboctahedral  $\text{A}^{[12]}$  positions are fully occupied by  $\text{Ce}^{3+}$  cations. The valence of these cations is compensated by 24  $\text{O}^{2-}$  and 128  $\text{N}^{3-}$  anions, so that 40 X positions of the perovskite superstructure are vacant. Therefore, the compound could also be formulated as  $\text{Ce}_{16}[\text{Si}^{[6]}\text{Si}_{14}^{[4]}\square(\text{O}_6\text{N}_{32}\square_{10})]$ , with  $Z = 4$ . The subarray of tetrahedrally coordinated Si atoms is represented in Fig. 20. This interpretation has been supported by the argument that the stability of the structure is primarily determined by the cations and that these maintain, in the oxonitridosilicate, the topology which is typical for the perovskite structures. This conclusion has led Liebau [107] to consider several other structures which had been previously described as ring silicates to be defect perovskites.

However, this description provokes an important question, i.e. why are the cationic vacancies where they are and not in other sites? Applying the Zintl-Klemm concept to this compound, the 64 Ce atoms and the 4 hexacoordinated Si atoms per unit cell, which act as donors, provide a total of 208 electrons. If we assume that 128  $e^-$  are captured by the 128 N atoms, these are converted into  $\Psi$ -O (this last argument should not be considered as a real



**Fig. 20** Stereopair showing the framework of tetrahedrally coordinated Si atoms in  $\text{Ce}_{16}[\text{Si}_{15}\text{O}_6\text{N}_{32}]$ . The framework is formed by three- and two-connected Si atoms as if they were  $\Psi$ -P and  $\Psi$ -S, in the ratio 4 : 3. The octahedrally coordinated Si atoms and the Ce atoms (all of them donors) have been omitted

process, it only means that each N atom needs one electron more than an O atom to satisfy its valence requirements). There remain 80 electrons per unit cell which can be transferred to the tetrahedral Si framework which is composed of 56 silicon atoms. The 24 Si(1) atoms, at the site  $24d$ , can accept  $2 e^-$  each (a total of  $48 e^-$ ) and are converted into  $\Psi$ -S atoms, with a twofold connectivity. The 24 Si(2) and 8 Si(3) atoms, at the sites  $24d$  and  $8c$  respectively, can accept  $1 e^-$  each and are converted into  $\Psi$ -P atoms (a total of  $32 e^-$ ). The resulting  $Si^{[4]}$  framework can be represented by the pseudo- $P_4S_3$  structure type, corresponding to three- and two-connected T atoms in the ratio 4 : 3. The O and N atoms are located near to the midpoints of the Si – Si contacts giving rise to the tetrahedral coordination observed in the T atom skeleton.

However, there exist some compounds which, at high pressures, produce structures with only hexa-coordinated silicon but in which silicon has an acceptor character. It can be shown that these structures can also be explained in the light of the Zintl–Klemm concept.

The first compound to be discussed is  $MgSiO_3$  which, under ambient P/T conditions, has a chain with the pyroxene structure in which all Si atoms have tetrahedral coordination and are two-connected:  $Mg_2^{[6]}\{ \infty^1 \} [Si_2^{[4]1;2}] O_6$  [110]. At high pressures and high temperatures, it transforms into an orthorhombically distorted perovskite [111] in which the Si atoms become octahedrally coordinated by O and the Mg atoms adopt an eightfold coordination:  $Mg^{[8]}\{ \infty^3 \} [Si^{[6]1;6}] O_3$ . This phase transition can be interpreted as an increase of the coordination number for both, Mg and Si, as a consequence of the application of pressure. However, in the light of the Zintl–Klemm concept, it can instead be interpreted as if the one-dimensional Si atom skeleton of the pyroxene chain, which is equivalent to the structure of fibrous sulfur, would have been transformed into the three-dimensional Si atom skeleton which is equivalent to the Te atom skeleton in  $TeO_3$  [112]. We have seen that, when the 8-N rule is applied, a  $\Psi$ -S atom forms two bonds. However, in the heavier elements of Group 16, such as Te, each atom can also use its six  $5s^2 5p^4$  valence electrons to form six bonds (simple cubic structure). Thus, a  $\Psi$ -S atom can use its six  $3s^2 3p^4$  valence electrons to form six two-centre, two-electron bonds with its six neighbours. The O atoms are then docked close to the six bonding pairs giving rise to the octahedral coordination. This interpretation of the perovskite structure has previously been reported [8] and theoretical calculations have also shown [113] that the defect perovskite structure is a stable one for the isoelectronic  $SO_3$ .

A corresponding phase transition at HP from  $Ca[Si^{[4]1;2}] O_3$  to perovskite-type  $Ca[Si^{[6]1;6}] O_3$  has been observed for  $CaSiO_3$  [102]. It is quite possible that it can also take place in  $SrSiO_3$  and  $BaSiO_3$ . In the case of  $BaSiO_3$ , the possibility of such a transition is supported by the fact that its BaSi subarray is of the CrB-type which, under pressure, undergoes the CrB-type  $\rightarrow$  CsCl-type transition as has been reported for  $KClO_3$  [114].

## 7

**Concluding Remarks**

As was stated for the aluminates [8], the structures just described and the above discussion clearly indicate that the Zintl–Klemm concept is maintained in the oxides and that the atoms forming the Zintl polyanions, behave structurally as real Zintl polyanions in spite of being embedded in an oxygen matrix. Following the term proposed by Parthé & Chabot [5], the Si atoms occupying tetrahedrally coordinated positions of the anion substructure can be considered as “cations ex-officio”. It seems clear that the application of the Zintl–Klemm concept can serve to rationalise and understand the skeletons of hundreds of silicates which had remained for many years at a descriptive level. The great number of similarities between the topology of the T-atom subarrays and the structures of Zintl polyanions clearly indicate that these similarities are not casual but they are new examples of how cations, in oxides, recognise themselves as previously shown for many other compounds [63].

One of the most interesting aspects of the above discussion is the rationalisation of the coordination number CN adopted by silicon in different compounds. It is well known that silicon normally appears as tetrahedrally coordinated and that the octahedral coordination should be regarded as an abnormal feature which has traditionally been attributed to the application of pressure. In this context the quartz  $\rightarrow$  stishovite transition has been explained and, in the same manner, the presence of hexa-coordinated silicon in the HP phases  $\text{Na}_2\text{Si}^{[6]}[\text{Si}_2^{[4]}\text{O}_7]$  [39],  $\text{K}_2\text{Si}^{[6]}[\text{Si}_3^{[4]}\text{O}_9]$  [52],  $\text{Na}_8\text{Si}^{[6]}[\text{Si}_6^{[4]}\text{O}_{18}]$  [53] and in  $\text{Na}_6\text{Si}_3^{[6]}[\text{Si}_9^{[4]}\text{O}_{27}]$  [54] could be understood. We see, however, that in the latter compounds both types of coordination polyhedra coexist and that this can be explained by an amphoteric behaviour of the Si atoms, i.e.  $\text{Si}^{[6]}$  acts as a donor whereas  $\text{Si}^{[4]}$  behaves as an acceptor producing the  $[\text{Si}_2\text{O}_7]^{6-}$ ,  $[\text{Si}_3\text{O}_9]^{6-}$ ,  $[\text{Si}_6\text{O}_{18}]^{12-}$  and  $[\text{Si}_9\text{O}_{27}]^{18-}$  anions respectively. It is true that the application of pressure can favour the donor character and hence an increase in the CN, but pressure should not be the only reason for it. In part, because pressure should produce the octahedral coordination for all the Si atoms, but also because the same structural features are present in  $\text{Ce}_{16}\text{Si}^{[6]}[\text{Si}_{14}^{[4]}\text{O}_6\text{N}_{32}]$  [109] which is not a high-pressure phase. We are aware that the coexistence of both types of coordination polyhedra in the same compound is a feature difficult to explain. It represents an important problem whose ultimate reasons need to be rationalised. We do not know at present which factors (electronic and geometric) determine this behaviour. However, the results just discussed seem to indicate that the formation of appropriate tetrahedral networks must be an important factor for the structure stabilisation. This can require, in some cases, the donor behaviour of some Si atoms. We have also seen how the difference in electronegativity is

an important factor which allows silicon to adopt an octahedral coordination in the presence of more electronegative tetrahedral atoms, as is the case in  $\text{Si}^{[6]}[\text{P}_2^{[4]}\text{O}_7]$  [103–107].

It should be remembered that the existence, and in some instances the coexistence, of both types of coordination polyhedra (octahedra and tetrahedra) was also present in aluminates [8]. There, it was discussed that the coordination number of the Al atoms was not a function of the size of the cation but rather a consequence of the atoms accompanying it in the structure and of the behaviour of the Al itself. The same can be said of silicon and silicates. The different CN values are difficult to explain if we are thinking of the existence of  $\text{Si}^{4+}$  cations. However, a rational insight is obtained if we think of the existence (or pre-existence) of the Zintl polyanions we have described. Again, the oxonitridosilicate  $\text{Ce}_{16}\text{Si}^{[6]}[\text{Si}_{14}^{[4]}\text{O}_6\text{N}_{32}]$  [109] provides a good example of this assertion. We have mentioned above that this compound was described as a perovskite variant with an ordered distribution of vacancies. Because similar defect perovskite structures can be recognised in many other silicates, it has been claimed that this arrangement can be considered as an expression of the strong stability of this structure type [107] and that this could be the reason for the appearance, against all expectations, of  $[\text{SiN}_6]$  octahedra. These considerations being valid, we believe that the principles applied here provide another explanation which accounts for the location of vacancies in the Si subnet. Thus, defects are not situated at random or located in arbitrary positions but they are situated in such a way that they produce the connectivity characteristic of a Zintl polyanion, in this specific case with pseudo-stoichiometry  $\text{P}_4\text{S}_3$ , which is that obtained if the valence electrons of both, cerium and octahedral silicon are transferred to the remaining Si atoms. It could be argued that the octahedral silicon atoms act as true cations whereas tetrahedral silicon acts as a cation *ex-officio*.

Other aspects of the structures discussed here, such as the location of the O atoms should also be considered. As we have seen, the O atoms are placed near both, the midpoints of the hypothetical Si – Si bonds and the lone pairs, producing a lack of linearity in the Si – O – Si bonds. The fact that the O atoms are normally situated close to (but not exactly at) the midpoint of a Si – Si bond produces the same effect as the rotation of the tetrahedra. This rotation was postulated [115] to derive the real structure of  $\beta$ -cristobalite ( $\bar{1}\bar{4}2d$ ) [116] from the non-existing ideal C9 structure. However, it is observed that, rather than tilting rigid  $[\text{SiO}_4]$  tetrahedra, the O atoms are located 0.5–0.6 Å off the centres of the elongated Si – Si bonds, thus producing Si – O – Si angles of around 140°. In fact, the Si array is topologically the same and has almost the same dimensions in both the tetragonal and the ideal C9 structures. It is true that the rotation of the tetrahedra has been experimentally observed as a continuous process when pressure is applied to the cristobalite-like compound  $\text{BPO}_4$  [117], however, this rotation cannot be claimed to account for the for-

mation of real cristobalite from a non-existing ideal C9 structure. When the structure is seen as derived from Si itself, it is unnecessary to postulate the existence of repulsive forces as responsible for the opening of the Si – O – Si angles, as concluded elsewhere [115].

Another related question is: why do O atoms respond in the same way to both the more delocalised bonding pairs and the more localised lone pairs. An answer to this question would be that the bonding pairs could also be forming non-nuclear maxima (NNM) between the two cations (bonded Si atoms). Regarding the possible existence of these NNM, it has been reported that their formation seems to be related to the application of pressure [118]. However, what can be concluded is that an  $O^{2-}$  anion seems to play the same role as a bonding electron pair.

Most of the compounds we have discussed can be better understood in the light of the Zintl–Klemm concept and Pearson's generalised octet rule. The connectivity between Si atoms is explained in all cases. In many of them, the Si atoms form skeletons identical to the corresponding Zintl polyanions. If no such Zintl polyanions are known, they should be energetically so favourable that their discovery is to be expected. It seems clear that these two old ideas, the Zintl–Klemm concept and Pearson's generalised octet rule, are neither exhausted nor out of date but can still serve to simplify and clarify structures which have not been explained otherwise.

The search is open to apply these principles to other families of compounds such as borates, gallates, germanates, phosphates and arsenates, among others. Probably, their application will allow us to put all these more or less unconnected structures on a common and universal basis. Another problem which remains unsolved is the physical meaning of the "cation recognition" that seems to exist in the oxides [8, 63]. We believe that this feature represents a challenge for theoretical chemistry which needs to be explained in the future.

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